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Rensselaer Polytechnic Inst., Troy, NY

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PREDICTING PREFERENTIAL ADSORPTION OF ORGANICS BY ACTIVATED CARBON

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By

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16. ABSTRACT

Preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions was studied to develope a comprehensive theoretical basis for predicting adsorption of multicomponent solutes. The research program investigates why some solutes are strong adsorbers, and others weak, and why some solutes displace others during aqueous phase adsorption. The overall objectives were to develop, test, and simplify the theoretical basis for prediction.

The fundamental multidimentional approach of the solvophobic thermodynamics theory was used to correlate the extent of adsorption for the comprehensive theory with the overall standard free energy change for the association adsorption reaction in solution, and for the simplified theory with the cavity surface area of the solute.

Experimental adsorption isotherms of two homologous series (alkyl phenols and alkyl alcohols) were measured and used to test the theory. Differences resulting from simple structural modifications of solutes were predicted theoretically and confirmed experimentally. Several experimental innovations for equilibrium adsorption studies have been introduced to reduce solute loss by extraneous adsorption and vaporization.

Small negative activation energies for intraparticle pore and surface diffusion of alkyl phenols were also calculated from a temperature study.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Although activated carbon adsorption has been widely used for color, taste, and odor removal in the water industry, only recently has it been considered seriously for the removal of *specific* dissolved organic compounds from water supplies. The work reported here is concerned with (1) developing a comprehensive theoretical basis for predicting the preferential adsorption of organic (homolog) compounds onto activated carbon from dilute solutions, and (2) measuring adsorption capacities to produce a data base with which to test the theory adequately.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

Preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions was studied to develop a comprehensive theoretical basis for predicting adsorption of multicomponent solutes. The research program investigates why some solutes are strong adsorbers, and others weak, and why some solutes displace others during aqueous phase adsorption. The overall objectives were to develop, test, and simplify the theoretical basis for prediction.

The fundamental, multidimensional approach of the solvophobic thermodynamic theory was used to correlate the extent of adsorption for the comprehensive theory with the overall standard free energy change for the association adsorption reaction in solution, and for the simplified theory with the cavity surface area of the solute.

Experimental adsorption isotherms of two homologous series (alkyl phenols and alkyl alcohols) were measured and used to test the theory. Differences resulting from simple structural modifications of solutes were predicted theoretically and confirmed experimentally. Several experimental innovations for equilibrium adsorption studies have been introduced, including the use of completely filled and capped stainless-steel centrifuge tubes that were attached to a rotating spindle and placed in a constant-temperature bath. After adsorption equilibrium was attained, the carbon particles were spun down in an ultracentrifuge. After the centrifuge cap was removed, the supernatant was sipped into a UV or TOC detector.

Intraparticle pore and surface diffusion coefficients of alkyl phenols were calculated by fitting the experimental data to a theoretical model using a graphical technique. Small negative activation energies for these diffusional processes were also calculated from a temperature study.

The theory was applied to bi- and penta-solute adsorption from homologous mixtures.

This report was submitted in fulfillment of Grant No. CR-806648-01 by Rensselaer Polytechnic Institute under sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 1, 1979, to December 31, 1981, and the work was completed on March 31, 1982.

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SECTION 1

INTRODUCTION

BACKGROUND

Although activated carbon (AC) adsorption has been used widely for odor and color removal in the water industry, only recently has it been seriously considered for removal of dissolved organics from water supplies [1]. This recent interest is caused primarily by the growing concern for potential carcinogenic, mutagenic, and teratogenic compounds found in drinking waters [2,3].

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Interest has recently intensified because of the U.S. Environmental Protection Agency (EPA) amendment of Part 141 of the National Interim Primary Drinking Water regulations, which establishes a maximum contaminant level for trihalomethanes (THM's) of 0.10 mg/l [4]. Furthermore, the amendment recommends granular activated carbon (GAC) for THM removal.

As a result of this interest, the National Academy of Science Subcommittee on Adsorption recently published a report on the evaluation of activated carbon for drinking water treatment [5]. A recent review of this report indicates that a predictive theory for preferential selectivity of different organics for AC adsorption is greatly needed [6]. In fact, many key questions are associated with the use of GAC and need further study. These include the possibility of biological regeneration, the action of microbes on adsorbed organics that are relatively resistant to biodegradation, the roles of ozone and chlorine in affecting microbial activity, the microbial generation of organic compounds during GAC treatment, the possible significance of catalysis during organics adsorption on GAC, the production of carbon fines that enter the product water, and the changes that may occur during the GAC regeneration process. In spite of this obvious lack of knowledge, EPA has proposed GAC as the recommended method for removing THM's from drinking water [4]. Few if any other processes have been suggested seriously for this application.

Additional background on GAC is reviewed by Belfort [7], including the important variables affecting adsorption and the current theories that are useful in predicting multicomponent competitive adsorption from single-solute isotherms.

The ability to predict the effects of even simple structural modifications on the adsorption of organic molecules from dilute aqueous solutions onto AC (or other adsorbents) could be of great value in the design and oper-

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ation of large-scale commercial water and wastewater treatment plants. Structural modifications such as those often found between isomers of the same homologous series are well known to make the difference between benign and toxic compounds [8]. At present, most theoretical approaches either rely on single-solute isotherms to predict mixed-solute isotherms, or they rely on solubility theory.

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OBJECTIVES

The objectives of this study were as follows:

1. To develop a comprehensive formalism of dilute aqueous-phase adsorption of organics, including fundamental formulations of all dominant interactions between solute, solvent, and sorbent.

2. To test the use of this formalism to predict a ranking order of adsorption capacity for members of homologous series.

3. To measure experimentally the equilibrium adsorption isotherms at constant pH and temperature for a statistically significant number of members of a homologous series.

4. To propose and apply certain simplifying assumptions to the comprehensive model that would result, for special cases, in a simplified analytical expression.

5. To compare correlations of adsorption capacity from the comprehensive and simplified theories with those obtained with other independent variables such as the molecular weight, density, index of refraction, molar volume, molar refraction, octanol-water partition coefficient, parachor, and polarizability.

6. To examine the possibilities of using the derived theory for predicting multi-component adsorption.

Objective 1 is fundamental to the other objectives. The theoretical formalisms developed during this study were tested both with experimental data obtained from the literature and that suggested in Objective 3. Objective 4 is crucial to the practicability and usefulness of the suggested approach. Objectives 5 and 6 were included because the usefulness of the theory will eventually depend on its ability to rank-order the adsorption of solutes with better predictability (i.e, higher linear coefficients of correlation) than other independent variables, and from multicomponent systems, respectively.

OTHER APPROACHES

With respect to solid-liquid adsorption, a major limitation of the various equilibrium theories of adsorption [9,10] is that they all were originally derived from gas- and vapor-phase adsorption, and thereby *a priori* ignored the presence of the solvent during adsorption of the solute. Also, single solute adsorption data are needed to predict multisolute competitive adsorp-

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tion, and other empirical mathematical equations represent the data without attempting to establish a physical model [10].

Freundlich, in his classic monograph [11], describes the first attempts 90 years ago by Traube and others to include the solvent-solute interaction effect through interfacial tension at the solid-liquid interface. Although Defay et al. updated this approach with a major emphasis on the simplified Gibbs adsorption model, especially under non-equilibrium conditions [12], a comprehensive interaction theory between solute, solvent, and sorbent was still lacking. Recent attempts to include the solvent-effect in aqueous phase adsorption include a semi-empirical approach based on partial solubility parameters called the net adsorption energy approach [13-15]. In spite of the limitations of this approach (see Ref. [9] for a detailed discussion), it does provide a useful qualitative screening method for estimating the relative adsorption capacity (rank order) of different organics.

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Although these approaches provide useful insight with respect to solute-solvent adsorption onto solids, the need exists for a comprehensive formalism of aqueous phase adsorption including fundamental formulations of all dominant interactions between solute, solvent and sorbent. The major goal of this study is to develop, test, and simplify such a comprehensive formalism for describing the *solvent effect* on the solute-solid adsorption association reaction.

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SECTION 2

CONCLUSIONS

The work reported here involves the development of a comprehensive theoretical basis for predicting the preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions. A detailed analysis of the effect of the solvent on this process yields an expression for the extent of adsorption with no adjustable constants. Branching, cyclization, and position isomerism are automatically accounted for without introducing additional terms or adjustable constants. In principal, the theory incorporates the variation of a wide span of experimental conditions, including a comparison of the adsorption of similar organic compounds on different activated carbons, and a comparison of the adsorption of different organic solutes on the same activated carbon. Under special conditions and assumptions, simplified analytical expressions result, allowing the prediction of the extent of adsorption as a function of the simple geometric characteristics of the (hydrocarbonaceous moieties) solute.

The solvophobic ($c\phi$) theory is tested using single-solute aqueous-phase adsorption isotherms of two homologous series. Homologous series of alkyl phenols and alkyl alcohols were chosen to represent aromatic and aliphatic organic groups in water, respectively. Correlations with adsorption capacity for both the comprehensive and the simplified $c\phi$-theories are compared with similar correlations for other independent variables, including molecular weight, density, index of refraction, molar volume, and group contribution parameters such as molar refraction (or polarizability), octanol-water partition coefficients, and parachor. For the 12-member alcohol homologous series, the best correlative parameters were the simplified $c\phi$-theory parameter, TSA ($r = 0.9263$) and the octanol-water partition coefficient, log P ($R = 0.9109$). All the other parameters had correlation coefficients of less than $r < 0.76$. For the 19-member alkyl phenol homologous series, TSA gave a higher correlation coefficient [$r = 0.88(2)$]than MW [$r = 0.87(9)$]. Fragmented isomers had higher adsorbabilities than their linear isomer. Surface orientation effects are proposed to explain this phenomenon.

As part of developing the comprehensive data base to test the theory, a new innovative procedure to measure batch adsorption isotherms was developed. The isotherms were measured at constant temperature and pH, and the procedure obviated the potential solute losses associated with the filtration step.

Besides determining the time to reach equilibrium, kinetic studies were conducted in detail for the alkyl phenols on powdered activated carbon (PAC).

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Both intraparticle pore and surface diffusion coefficients were calculated by fitting the experimental data to a theoretical model using a graphical technique. Excellent correlations between these diffusion coefficients and cavity surface area (TSA) are obtained. Two simultaneously competing phenomena (self-diffusion and the exothermic adsorption process) are thought to affect the intraparticle diffusion processes as a function of temperature. Small negative activation energies result from Arrhenius plots.

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Although several approaches are compared for predicting bisolute adsorption from single pure adsorption isotherms of propyl phenol and phenol, the major result obtained for pentasolute adsorption from the cϕ-theory suggests that a multi-step procedure based on surface tension could be used to predict the adsorption of each solute in the mixture.

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SECTION 3

RECOMMENDATIONS

We recommend that both the theoretical formulations and the experimental data base be extended with the objective of expanding the comprehensive theoretical solvophobic ($c\phi$) model for predicting a priori the preferential adsorption of organic compounds on activated carbon from aqueous solutions.

With the use of a detailed thermodynamic analysis of the effect of the solvent on the adsorption association reaction, the solvophobic ($c\phi$) interaction approach has been adapted and tested for predicting the extent of adsorption for several homologous groups both with data from the literature [16,17] and data measured during this study. Both the comprehensive and simplified versions of the $c\phi$-theory have given very encouraging results. The $c\phi$-theory nevertheless needs to be further developed and extended to include the adsorption of nonpolar, polar, and charged solutes and competitive adsorption. The $c\phi$-theory should also be extended to include explicit expressions for the free energies associated with polymers ΔG_{mix}, the reduction term, ΔG_{red}, and the gas-phase term, ΔG_{gas}.

By measuring the gas-phase adsorption of the same homologous series of compounds as that measured from the liquid-phase, $\Delta G^{net}_{(solvent\ effect)}$ could be directly measured [see later, Eq(5)]. The validity of some assumptions (those on which the adaptation of the solvophobic theory to adsorption is based) could be checked. With the study of additional homologous series and the knowledge of the molecular structure and volume of each member, the restriction of adsorption because of steric hinderance, as recently suggested by Benedek (slow adsorption), could be determined. Further work is also necessary to couple the theory to Myers' new characteristic dimensionless adsorption parameter.

With respect to equilibrium adsorption isotherm measurements, the limited data base should be extended to include a comparison of different activated carbons with different pore sizes and surface activities. Adsorption of ionizable homologous groups should also be measured. Competitive adsorption effects should be extended to include additional homologous series. Finally, we recommend that the theory be evaluated for competitive adsorption of some industrial effluent streams, such as coal-based effluents containing many isomers of phenols.

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SECTION 4

EXPERIMENTAL

CHARACTERIZATION OF SORBENTS

The sorbent properties are presented in Table 1 and the frequency distributions of pore volumes versus pore diameters are shown in Fig. 1.

The granular activated carbon (GAC) was obtained from sample stock of known specifications and ground into a powder (PAC) for adsorption studies. The carbon black was "graphitized" by heating, in the absence of air, to 2700°C. Since there is little evidence of fine porosity in graphitized blacks, the surface area measurements by nitrogen adsorption isotherm probably represent the geometric surface area.

The nitrogen adsorption characterization studies were performed in a surface-area pore-volume analyzer (Model 2100E, Micrometrics Inst. Corp., GA). Although the data for N_2 adsorption and desorption were fitted to several models, Langmuir, Dubinin-Polyani, and B.E.T., only results from the B.E.T. model are reported in Table 1 for comparison with data from the literature.

Grinding the GAC into PAC reduces the available surface area to N_2 by 1.75%. This is probably not significant and is within the error of the measurement technique. The graphitized carbon black is without internal porosity and has greater than one order of magnitude lower surface area than the PAC.

In Fig. 1a and 1c, it can be seen that greater than 70% of the pore volume during N_2 adsorption is below pore diameters of about 60Å for the GAC and the PAC. Between 8 and 20% of the volume is found in larger pores up to 250 and 500Å, respectively. Because of hysteresis effects, about 25% of the volume fraction appears to be shifted to the larger pore-sizes (>100Å) during N_2-desorption (see Fig. 1b and 1d).

ADSORBATES

All the chemicals used in this study were of the highest grade (>99% purity). The alkyl phenols were obtained from Supelco, (PA) and the alcohols from the Aldrich Co. (Wisc.). Stock solutions of the individual compounds were made up with standard 0.01m phosphate buffer and stored in amber glass or aluminum covered bottles at pH = 7.0.

Alkyl phenols were chosen as the first homologous series of adsorbates to be studied in this project for the following reasons:

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TABLE 1. PROPERTIES OF ADSORBENTS

Property	Activated carbon		Graphitized carbon (Nonporous)
	Granular (Microporous)	Powdered (Microporous)	
Surface area, m^2/g (N_2, B.E.T. Method)	1031	1031	89(107)*
Pore volume, cm^3/g	0.95	0.95	No pores
Equivalent particle diameter, μm	1190 ± 600	37.0 - 74.0†	37.0 - 74.0†
Bulk density, g/cm^3	0.478*	0.478*	0.353*
Trade name	Filtrasorb 400	Filtrasorb 400	Graphitized Vulcan 6
Manufacturer	Calgon Corp., Pittsburgh, PA	Calgon Corp., Pittsburgh, PA	Cabot Corp., Billerica, Mass.

* Reported value by manufacturer.

† US Sieve Series no. 200 to No. 400 range.

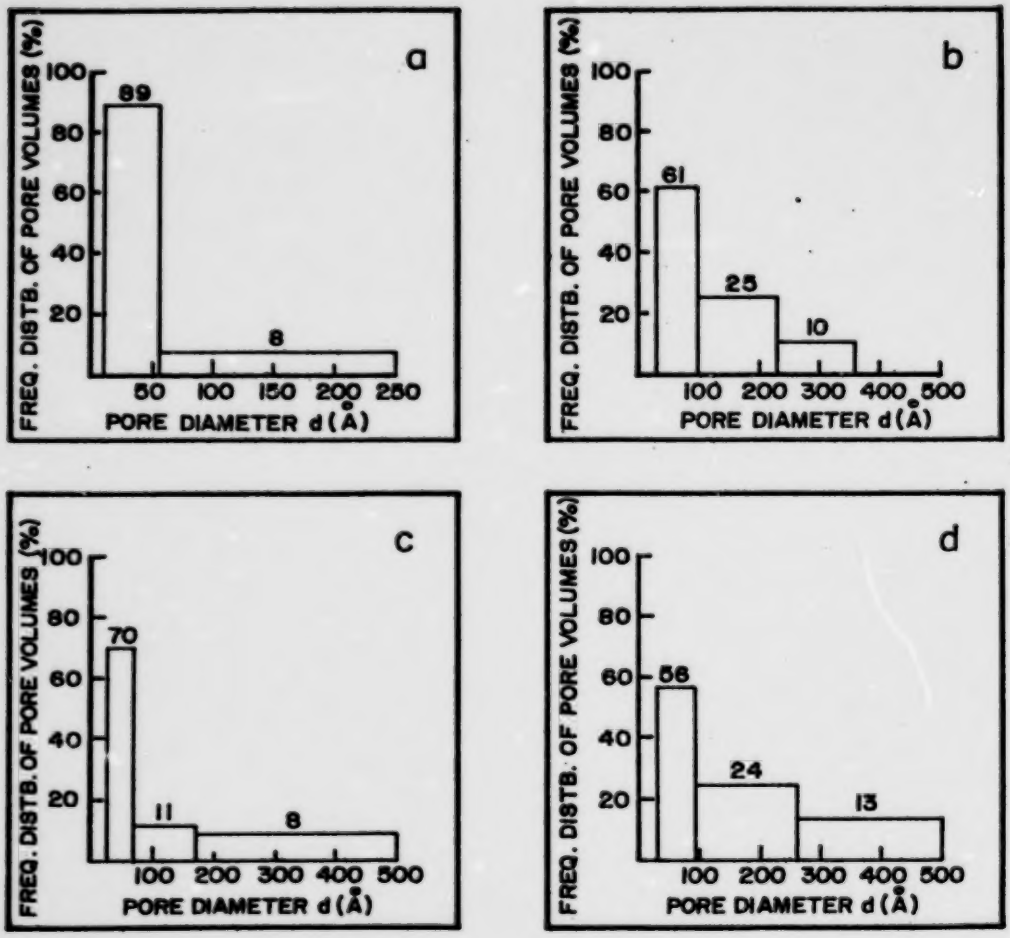

Fig. 1 Frequency distribution of pore volume versus pore diameter during nitrogen adsorption (a,c) and desorption (b,d) for GAC (a,b) and PAC (c,d).

a) Alkyl phenols are widely found in coal-conversion process wastewaters [18].

b) Singer and Yen [19] studied the adsorption of several of the same compounds on a new very high surface area PAC (designated as PX-21 with 2800-3500 m^2/g). Although, the current study evaluates a widely used commercial activated carbon (Filtrasorb-400), results from Singer and Yen's work could be used as a baseline. Correlations of the adsorption capacity from their work with the solvophobic theory were very encouraging (see Fig. 11, Ref [16]).

c) Alkyl phenols are relatively easy to measure by UV spectroscopy as single adsorbates.

d) Alkyl phenols are commercially available as a homologous series of compounds. Fundamentally they are interesting since as the length of the alkyl group is increased aromaticity decreases with increased aliphaticity. The aliphatic groups can be branched and fragmented allowing these properties to also be studied.

e) Because of their characteristic 107 mass peak in mass spectrometry the amount of alkyl phenols are easily quantified from mixtures after separation by GC. (The solutes are first extracted from the aqueous phase by methylene chloride).

Alkyl alcohols were chosen as the second homologous series of adsorbates to be studied in this project because:

a) They are frequently found in industrial effluents resulting from their wide use as solvents and reactants,

b) They are commercially available as a homologous series of linear and branched compounds. Fundamentally they are interesting because many isomers of the same molecular weight can be studied for branching effects and position of hydroxyl groups, and,

c) They are relatively easy to measure by total organic carbon analysis (TOC) as single adsorbates.

PRETREATMENT OF THE SORBENTS

Both the as-received granular activated carbon and the graphitized carbon were ground in a jar-mill for several hours until the entire carbon samples passed through a U.S. Sieve Series No. 200 (sieve opening 0.074 mm) and were retained by a U.S. Sieve Series No. 400 (sieve opening 0.037 mm).

The entire samples were then washed four times with deionized bacteria-free water to remove extraneous solutes such as salts or colloids. The samples were magnetically stirred in 9-ℓ glass carboys and the wastewater decanted and replaced every 24 hours. After the last washing, the water was decanted and the carbon samples placed in a vacuum oven (Isotemp. No. 281, Fisher Scientific, N.Y.) at 100°C and 25 mm Hg vacuum for about 5 days until

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dry. The oven temperature was then increased to 120°C to remove extraneous volatile organics until constant weight was attained. The samples were then stored over CaO in a desiccator.

About 48 hours before use, the carbon was placed into autoclaved deionized water and stored in a 1-ℓ amber glass bottle in the dark to allow complete water adsorption.

KINETIC STUDIES

The primary reason for conducting the kinetic studies was to determine the minimum period needed to attain equilibrium for the adsorption isotherms.

Several 38mℓ stainless steel centrifuge tubes (Part No. 301112, Beckman, CA) were filled with a fixed volume of aqueous solution containing a known concentration of a specific solute and with the same carbon dosage. The tubes were attached to the rotating (360°) mixer and placed in a constant temperature (20 ± 0.5°C) water-bath. At various intervals tubes were removed from the bath and the residual solute concentration in the bulk solution determined.

Since the rate of solute uptake for several solutes was faster than the processing time to centrifuge the sample, the usual filtration technique to remove the carbon from the fluid was also used. After filtering through a 0.45μm cellulose nitrate filter, the filtrate was analyzed by UV spectroscopy (Model 552, Perkin Elmer, N.J.) for the alkyl phenols. A plot of normalized bulk solute concentration versus time provided the information needed for the adsorption isotherms and kinetic analysis. These data are presented later.

ADSORPTION ISOTHERM PROCEDURE

Several innovations have been introduced into the adsorption isotherm procedures in an attempt to improve reproducibility and accuracy and reduce solute losses. Although there is a widely held view among some water technologists that liquid-phase adsorption is relatively insensitive to temperature, and therefore need not be accurately controlled, temperature was kept constant at 20 ± 0.5°C during this study. The pH was also buffered at 7.0 ± 0.1 with standard 0.01M phosphate buffer.

To minimize extraneous solute-loss and maximize solute/sorbent contact the following steps and precautions were taken:

a) Adsorption was conducted in completely filled and capped 38-mℓ stainless-steel centrifuge tubes (Part No. 301112, Beckman, CA). Thus there was no head-space for possible solute loss to the gas phase, and the solutions were only exposed to stainless steel surfaces for both minimum adsorption loss and to reduce the possibility of introducing extraneous organics.

b) The completely filled tubes were rotated end-over-end 360° at 2 rpm in a constant-temperature bath (20 ± 0.5°C; see Fig.2). This allowed the carbon to fall the length of the tube twice per rotation resulting in good mixing and increased effective external film mass transfer coefficient. The

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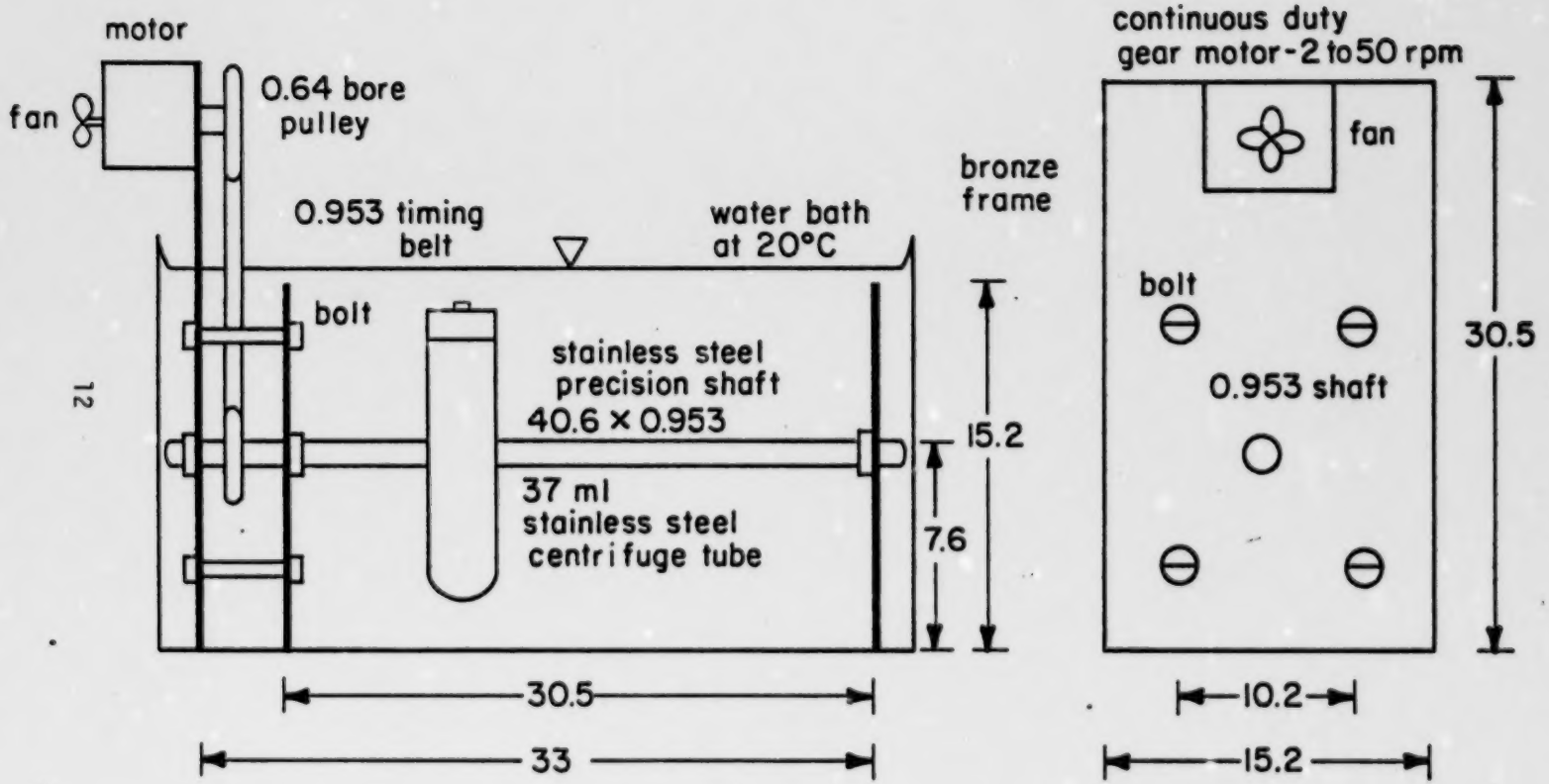

Fig. 2. Water bath (T = 20± 1.0°C) and rotary mixer (dimensions in cm).

time to reach equilibrium varied from two to several hours depending on the kinetics of the particular solute and rotation rate. The mixing period employed in this study was 24 hours for most solutes.

c) Once equilibrium was attained, the tubes were placed directly into an ultracentrifuge (Model L8-55, Beckman, CA) and the carbon was spun-down at 20,000 rpm for 20 min.

d) The residual solute concentration was measured from aliquots of the supernatant by UV-spectroscopy (Model 552, Perkin Elmer, N.J.) or TOC(Model 915A, Beckman, CA). UV spectroscopy was used for measuring the alkyl phenol concentrations. An automatic sipping device run by a positive displacement pump (and not by vacuum suction) was used to measure the solution solute concentration directly from the centrifuge tube. The maximum absorbance wavelength was determined for each alkly phenol and a corresponding calibration curve of absorbance versus concentration was prepared. A detectable limit of about 0.2 ppm was achieved.

Total organic carbon analysis (TOC) was used for measuring residual alcohol concentrations. A calibration curve was prepared from standard stock solutions before each analysis. A detectable limit of 0.5 ppm was achieved.

To identify individual solutes from a mixture of alkyl phenols, the solutes were extracted with methylene chloride, separated in the gas chromatograph (Signa 4, Perkin Elmer, N.J.) and quantified in a mass spectrometer (Model 1020, Finnigan, CA).

DATA ANALYSIS

All the raw adsorption data have been retained in computer files. Although the single solute date from this study have been fitted to the Langmuir model

$$Q = \frac{Q^o bC}{1 + bC} \qquad (1)$$

where Q is the amount adsorbed(in mmoles/g)and C is the equilibrium solution concentration (in mmoles/L), it could just as easily be fitted to any other suitable model. Q^o is the asymptotic saturation value of Q and b is the energy-related constant. The linearized form of the model

$$\frac{1}{Q} = \frac{1}{Q^o b}\frac{1}{C} + \frac{1}{Q^o} \qquad (2)$$

is used to describe the data. The natural log of the reciprocal of the slope ($\ln Q^o b$) is used to describe the region of the adsorption isotherm defined by Henry's Law for liquids.

The Langmuir model is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent

surface, the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface. A computer program was written for this and several other single-solute adsorption models. The reason for using the Langmuir model was that it correlated the data as well as other models (Freundlich) and has the desired Henry's limit at low concentrations.

STATISTICAL ANALYSIS

Given a bivariate normal distribution of n pairs of observations x and y, it is often of interest to determine whether or not the two variables are stochastically dependent. The correlation coefficient r is a measure of this dependence. Its value can lie between minus one and plus one. If it amounts to either minus one or plus one, the two variables totally depend on one another. If its value is zero, the variables are stochastically independent of one another.

More commonly, the correlation coefficient gives a value somewhere between zero and plus or minus one. To verify that the measured value of r is statistically not equal to zero, we must test the hypothesis $r = 0$ against the alternative that r does not equal zero. When $r = 0$ it can be shown that

$$t = r[(n-2)/(1-r^2)]^{1/2} \qquad (3)$$

is distributed as the Student's t distribution with n-2 degrees of freedom [20]. The hypothesis can therefore be tested against the critical value of t for the specified degrees of freedom.

We can also test the hypothesis that r is equal to some value other than zero. Testing the hypothesis that $r_1 = r_2$ is effected by means of the quotient.

$$\frac{z_1 - z_2}{[1/(n_1-3) + 1/(n_2-3)]^{1/2}}$$

which follows approximately the unit normal distribution; $z_1 = \tanh^{-1} r_i$. this value can then be tested against the appropriate significance limit to verify or reject the hypothesis [20].

In addition, a statistical comparison of several correlations can also be performed to test the hypothesis $r_1 = r_2 = \ldots = r_k$. This comparison is effected by means of the test statistic $\Sigma(n_i-3)(z_i-\bar{z})^2$ significance limit χ^2 at a specified confidence limit for $k = 1$ degrees of freedom, where

$$\bar{z} = \sum_1^k (n_i - 3)\, z_i / \sum_1^k (n_i-3) \qquad (4)$$

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SECTION 5

THEORETICAL

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GENERAL SOLVOPHOBIC APPROACH

The solvophobic ($c\phi$) theory describes the tendency of a surrounding solvent medium to influence aggregation or dissociation of molecules with considerable microsurface areas exposed to the solvent medium. Examples of these molecules include amino acids, nucleotide bases in biopolmers, various drug molecules, antigens and substrates, and relatively low molecular weight organic homologues and an adsorption surface. The $c\phi$-theory has also introduced a new measurable quantity called "the thermodynamic microsurface area change of a reaction" [21] which is now finding applications in protein structure [22], high performance liquid chromatography [23], protein salting-in and salting-out [24], the conformational structure of organic compounds [25], isomerization reactions [26], stacking of bases and solvent denaturation of DNA [27], and association adsorption reactions [16].

The approach used here follows closely that used by Belfort [16] in which he adapted the $c\phi$-theory, originally presented by Sinanoğlu [28] and applied to HPLC by Horvath et al. [23], to the association adsorption reaction. For a comprehensive review of the adaption of this approach to the adsorption of organic substances from dilute aqueous solutions by non-polar adsorbents, the reader is referred to the literature [9,16,29]. Since this is an equilibrium theory, kinetic effects such as convective mass transfer and solute diffusion processes are not considered.

In the solvophobic treatment, adsorption is considered as a reversible reaction between the adsorbate molecules S_i and the activated carbon C, to form the adsorbed complex, S_iC at the surface of the carbon, $S_i + C \rightleftarrows S_iC$. The effect of the solvent on this reaction is obtained by subtracting the standard free energy change for the reaction in the gas phase from that in the presence of the solvent (taking as standard states $X_k^\circ \equiv 1$, $p_k^\circ \equiv 1$ atmosphere ideal gas). This process is shown diagramatically in Fig.3, and results in a net free energy change, $\Delta G^{net}_{(solvent\ effect)}$, expressing the

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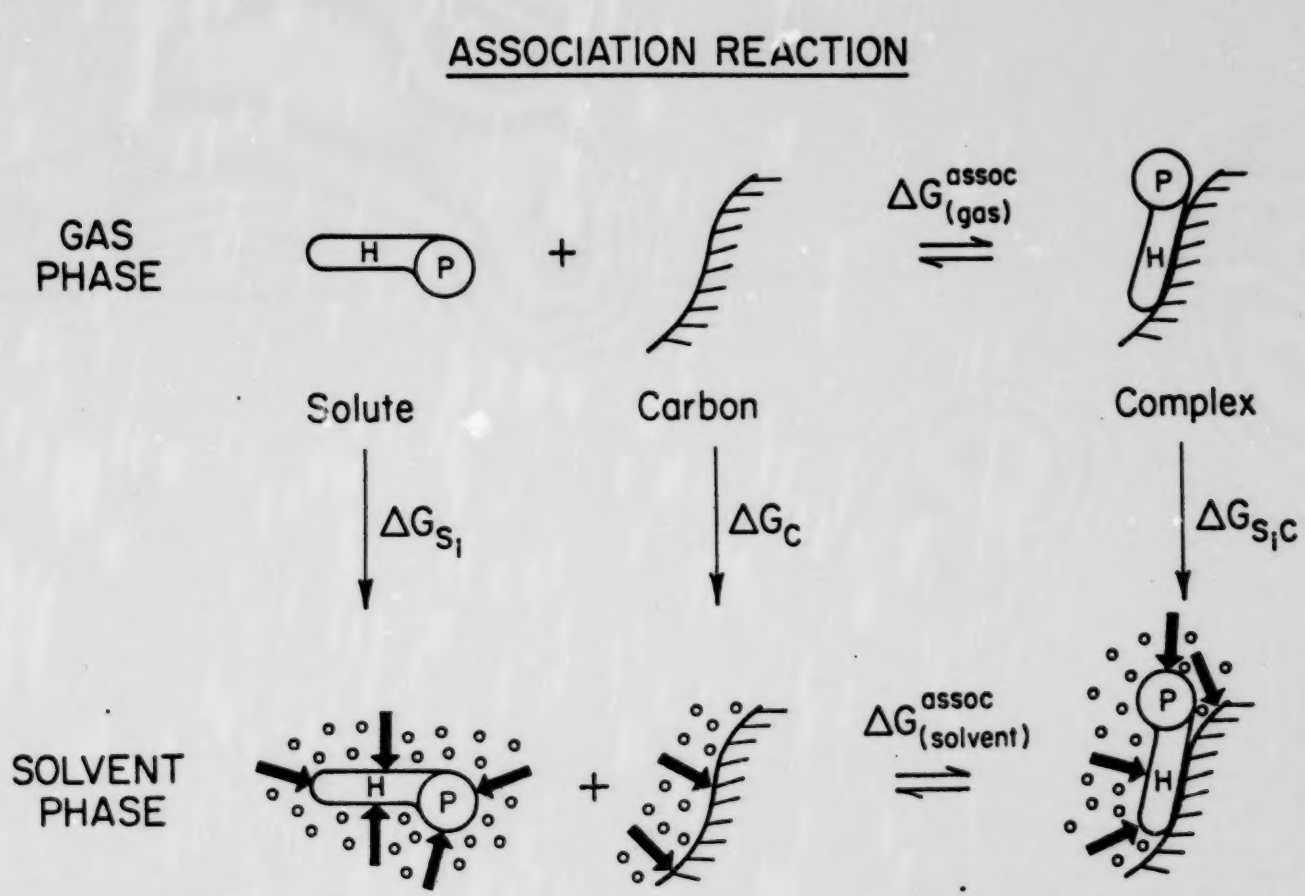

Fig. 3. Pictorial representation of the association adsorption reaction in the gas and solvent phase.

effect of the solvent on the association adsorption reaction.

COMPREHENSIVE MODEL

Conceptually, Sinanoğlu proposed a two-step dissolution process [28]. First, a hole or cavity needs to be prepared in the solvent to accommodate the solute, carbon or adsorbed complex "molecule". Second, after the "molecule" is placed into the cavity, it interacts with the solvent. Quantitatively this process is expressed as follows:

$$\Delta G^{net}_{(solvent\ effect)} = \Delta G^{assoc}_{(solvent)} - \Delta G^{assoc}_{(gas)} = RT\ \ell n[k^H_{S_iC}/k^H_{S_i}k_C{}^H] \quad (5)$$

or

$$\Delta G^{net}_{(solvent\ effect)} = \Delta G^{net}_{j,S_iC} - \Delta G^{net}_{j,S_i} - \Delta G^{net}_{j,C} \quad (6)$$

where $k^H_k = p_k/\chi_k$, are the Henry's constants for the k^{th} species, and j represents each type of interaction. After specifying each interaction such as the cavity, van der Waal's, and electrostatic terms plus two correction terms for polymer mixing and reduced electrostatic effects due to the presence of the solvent, the following expression is obtained from Eqns (5) and (8) for the overall standard free energy change, viz

$$\Delta G^{assoc}_{(solvent)} = \Delta G^{assoc}_{(gas)} + [\Delta G_{cav} + \Delta G_{vdw} + \Delta G_{es} + \Delta G_{red}]^{net}_{S_iC\text{-}S_i\text{-}C} - RT\ \ell n\ (RT/P_oV) \quad (7)$$

where the last term is called the cratic term and results from an entropy or free volume reduction. $\Delta G^{assoc}_{(solvent)}$ is related to the experimental equilibrium constant $K_{solvent,i} = \chi_{S_iC}/\chi_{S_i}\chi_C$ which itself will be related to the experimental adsorption capacity $\bar{p}_i$ for solute S_i later in this analysis. Each term in the square bracket in Eqn (7) can be calculated explicitly from known physicochemical parameters obtained from the literature [30]. Explicit formulae to do this and a discussion on the relevance of each term to the adsorption association reaction is presented in Appendix A. The dominant

interactive forces and important parameters for each interactive process are, however, summarized in Table 2.

For non-polymer molecules where Henry's law is expected to hold, the correction ΔG^{net}_{mix} can be neglected in Eqn (7). The dispersion correction for the presence of water ΔG^{net}_{red} is only relevant to the adsorbed complex S_iC, and although it can vary in value by about 15-30% of the ΔG^{net}_{vdw}, S_iC value, it is probably fairly constant for a homologous series and will thus be neglected in the present calculations. Also, the solute-sorbent gas phase interaction, $\Delta G^{assoc}_{(gas)}$, can, in general, include van der Waals, electrostatic, hydrogen-bonding, or covalent interactions. For a homologous series, this term is thought to vary negligibly and is thus considered constant in the present analysis.

Because of the association adsorption reaction of solute S_i onto sorbent C, the total surface area in contact with the free solvent is reduced by the contact surface area.

$$\Delta A = A_{S_i} + A_C - A_{S_iC}. \qquad (8)$$

As mentioned earlier, Sinanoglu calls this "the thermodynamic microsurface area change of the reaction" [21].

With respect to the activated carbon surface essentially two types of surface interactions are thought to predominate. The first type of surface interaction, which occurs on most of the available surface area (on basal planes), can be characterized by van der Waals' physical interactions, and is apolar in nature. The second type of surface interaction, which occurs at the more reactive edges of the microcrystallites, can be characterized by positive physical(and maybe even chemical) attractive interactions due to hydrogen bonding and electrostatic forces. Although the second type of surface interaction probably occurs at a small fraction of the total surface area, the specific adsorptions result from the surface heterogeneity and to the presence of oxides, hydroxyls, and other groups on the surface. Adsorption differences between AC'S made from different raw materials (wood, lignite, coal, bone petroleum residues and nut shells) is probably the result of their different energy potential and the extent of

TABLE 2. INTERACTIVE FREE ENERGY CHANGES

Interaction process	Free energy designation	Interaction forces	Important parameters
Cavity formation	$\Delta G^{net}_{cav,i}$	Surface forces	Solute molecular surface area, TSA corrected macroscopic surface tension, γ_f
Solvent-solute interaction			
Van der Waal's	$\Delta G^{net}_{vdw,i}$	Dispersive (attractive) forces	Ionization potential and molecular volume v_f
Electrostatic	$\Delta G^{net}_{es,i}$	Electrostatic interaction	Inverse molecular volume, v_f (a) Simple dipole. Solute dipole moment μ_i and dielectric constant of solvent ϵ (b) Charged species. Ionic charge ze and ionic strength, I
Mixing effects (polymers)	ΔG^{net}_{mix}	Free energy of mixing	
Dispersive reduction as a result of solvent	ΔG^{net}_{red}	Masking of the dispersive forces	
Free volume reduction (cratic)	$RT\ \ell n\ (RT/PV)$	Entropic reduction	Solvent molar volume V and pressure P

these heterogeneous sites. Since hydrophobic or apolar interactions play a dominant role in AC adsorption of nonpolar (or nonpolar moieties of) solutes, the reduction in area ΔA given in Eqn. (4) is most likely the results of the first type of interaction discussed above.

After substituting for each relevant free energy term in Eqn. (7) and making simplifying assumptions detailed in Appendix A, the standard unitary free energy change for the overall process is given by

$$\Delta G^{assoc}_{(solvent)} = \Delta G^{assoc}_{(gas)} - \Delta G_{vdw,S_i} + \Delta G_{es,S_i} - N\gamma\Delta A - N\gamma V^{2/3}(K^e-1)\frac{A_{S_i}}{V_i^{2/3}} - RT \ln RT/(P_o V) \quad (9)$$

In applying the solvophobic theory to cis-trans isomerization of azobenzene in several solvents, Halicioglu and Sinanoğlu [26], calculated each of the terms in Eqn. (9) without the use of an adjustable parameter. In most cases, they found that the solvation of *inverse volume forces* [fifth term on the right hand side of Eqn. (9)] and the *surface forces* [fourth term on the right hand side of Eqn. (9)] both strongly affect the molecular association equilibrium or rate constants. The treatment indicates that these two solvent effects usually oppose each other. For small solute molecules relative to the size of the solvent molecules, the solvation or *inverse volume forces* may dominate; however, as the relative size of the solute molecules increases, *surface forces* may predominate [26,28,31].

Before simplifying the comprehensive model expressed through Eqn. (9), it is appropriate to note that

$$\Delta G^{assoc}_{\substack{(solvent)\\(gas)}} = RT \ln K_{\substack{solvent,i\\gas,i}} \text{ (unitary)} \quad (10)$$

where

$$K_{solvent,i} = X_{S_i C}/(X_{S_i} X_C) \text{ or } K_{gas,_i} = P_{S_i C}/(P_{S_i} P_C) \quad (11)$$

for dilute solutions assuming $a_i \simeq X_i$ and $\gamma_i \equiv 1$.

SIMPLIFIED MODEL

In considering Eqn. (9) at least two special cases of interest are relevant for aqueous-phase AC adsorption studies. The first case concerns the adsorption on *different* AC *surfaces* (i.e. different types of AC) of the same organic compounds at constant temperature, composition, and flow conditions. Although the theoretical expressions for this case are available [16], they have not been tested with data yet. The second case and the one of interest here concerns the adsorption of *different solutes*, such as those belonging to various homologous series, at constant temperature and flow rate and with the same solvent and carbon. For this case the standard unitary free energy change in the solvent is given by the following expression for

$$\Delta G^{assoc}_{(solvent)} \equiv K'_1 + \Delta G_{es,i} - K'_2 \Delta A \qquad (12)$$

where the constants K'_j are given by

$$K'_1 = \Delta G^{assoc}_{(gas)} - \Delta G_{vdw,i} - N\gamma V^{2/3}(K^e-1)\frac{A_i}{V_i^{2/3}} - RT \ln RT/(P_o V) \qquad (13)$$

$$K'_2 = N\gamma \qquad (14)$$

From Eqns. (6), (10) and (11), the relationship between the equilibrium constant for unitary adsorption from the liquid phase, $K_{solvent,i}$ and that from the gas-phase, $K_{gas,i}$ may be obtained as a function of the net free energy for the solvent effect, i.e.

$$K_{solvent,i} = K_{gas,i} \exp\left[\Delta G^{net}_{(solvent,\ effect)}/RT\right] \qquad (15)$$

To verify this theory experimentally, the equilibrium coefficient $K_{solvent,i}$ must be related to a measurable adsorption capacity $\bar{p}_i$, characteristic of species i for the entire adsorption isotherm. Unfortunately at present, no single parameter is considered reliable in characterizing the entire adsorption isotherm. However, Myers and Sircar have recently suggested that the free energy of immersion on placing a sorbent into the pure liquid phase solute, ΔG_{im}, could be used with the saturated adsorption capacity, Q^o, to characterize this association reaction and to transform the

polanyi potential into a dimensionless function which should be the same for all adsorbates in a given adsorbent [32]. Although ΔG_{im} should be obtainable from the cϕ-theory directly, further work in this area is necessary.

SURFACE TENSION AND AQUEOUS ADSORPTION

In this section, an alternate theoretical approach to that developed by Sinanoğlu [28] and used by others [23,33] is presented. This approach circumvents several previous difficulties concerning the curvature correction for the surface tension which was estimated for aqueous solutions from a correlation of nonpolar liquids [31], and which appears to fall away for quasi-spherical solute molecules [17].

Assuming that the activated carbon surface is essentially nonpolar in character, that the major mechanism of the adsorption process is the result of hydrophobic interactions, and that the surface tension of the solvent in contact with the adsorbed complex is approximately equal to that in contact with the carbon, the following revised expression for the standard unitary free energy change for the overall process is obtained

$$\Delta G^{assoc}_{(solvent)} = \Delta G^{assoc}_{(gas)} - \Delta G_{vdw,s_i} + \frac{N(\lambda-1)}{2\lambda}\frac{\mu^2_{s_i}}{\nu_{s_i}} DP + N\gamma_{wh}[(1-q)-g]A_{h,s_i} - RT \ln RT/(P_o V) \quad (16)$$

where $q = \gamma_{wh,s_i}/\gamma_{wh}$ and the ratio of the contact area to hydrocarbonaceous (hydrophobic) area is given by $q = \Delta A_h/A_{h,s_i}$. Thus, through q the curvature corrections enters the expression explicitly. q is approximated by [34]

$$q = [1 + \frac{2}{R_i}]^{-1} \quad (17)$$

where R_i is the molecular radius, Å and approximated by $(A_i/4\pi)^{1/2}$ for a sphere, A_i is either the total area (TSA) or hydrocarbonaceous surface area (HSA), $Å^2$. By relating $\Delta G^{assoc}_{(solvent)}$ given by Eqn. (10), via the equilibrium constant $K_{solvent,i}$, to the observable adsorption capacity coefficient $\ln \bar{p}_i$, the following is obtained for the simplified cϕ-theory [35]:

$$\text{Log } \bar{p}_i = m A_i + \text{constant} \qquad (18)$$

where $m = -\frac{N\gamma_{wh}}{RT}[(1-q)-g]$. From a plot of log $\bar{p}_i$ verses A_i, the slope m and g are obtained directly with the help of Eqn. (18) and a value of γ_{wh}, the interfacial tension between water and a hydrophobic surface [36].

Earlier, Eqn (9) was developed to calculate the free energy change for the adsorption of a dilute single solute of an homologous series. Here it is used to compare the adsorbability of an homologous series of solutes singly and in competition.

In addition to relating the hydrophobic surface area to adsorbability, Eqn (18) also suggests how the surface tension of an aqueous solution effects the adsorbability of a single solute. While γ_{wh}, the interfacial tension between water and the hydrophobic moeity is not easily measured directly, it can be considered proportional to the solution-air interfacial tension (here, the air interface serves as a hydrophobic surface).

This relationship was tested by measuring the isotherms of a 2-butyl phenol in the presence of small amounts of methanol. The methanol served to lower the surface tension of the bulk solution, while not being adsorbed itself in any detectable amounts.

This approach also suggests that competitive adsorption might be related to the surface tension of a multi-component solution. The variable f* may be defined as follows:

$$f_i \equiv \frac{\Delta_i}{\Delta_m} \equiv \frac{\left[\frac{\gamma-\gamma_i}{\gamma}\right]}{\left[\frac{\gamma-\gamma_m}{\gamma}\right]} = \frac{\gamma-\gamma_i}{\gamma-\gamma_m} \qquad (19)$$

Where

γ = surface tension of water, dynes cm^{-2}

γ_i = surface tension of saturated solution of single solute i, dynes cm^{-2}

γ_m = surface tension of solution containing all solutes to be adsorbed, dynes cm^{-2}

Also, a variable ζ may be defined as

$$\zeta = \frac{\log (Q^\circ b)_i^m}{\log (Q^\circ b)_i} \qquad (20)$$

where superscript m refers to the adsorption of the i^{th} solute from the mixture.

If the correlation of ζ_i vs. f_i is known, then the multi-component adsorption of solutes belonging to the same homologous series may be predicted in the following manner.

1. Measure γ_m for the mixture and obtain from a handbook γ_i for each identified single solute.
2. Calculate f_i.
3. Measure or obtain from literature single solute isotherms and get $(Q^\circ b)_i$.
4. From correlation calculate $\log (Q^\circ b)_i^m$.

EQUILIBRIUM ADSORPTION ISOTHERMS

Many well-known and not so well-known expressions have been formulated to describe single solute adsorption from gas and liquid phases onto liquid and solid surfaces. Some of these models are based on a proposed physical description of the adsorption process (e.g. Polanyi, Langmuir and BET), while other models are empirical in nature (Freudlich). For an assessment of equilibrium theories as applied to single and multi-solute liquid phase adsorption onto activated carbon, see Reference [10].

A general empirical equation for calculating the adsorption equilibria of organic solutes in aqueous solutions has been proposed (37-40), viz.

$$Y_i = \frac{a_{io} X_i^{b_{io}}}{c_i + \sum_{j=1}^{n} a_{ij} X_j^{b_{ij}}} \qquad (21)$$

where Y_i is the amount of solute i, adsorbed per unit weight of carbon at equilibrium concentration X_i in a solution containing n solutes. X_i and X_j represent the equilibrium concentrations for solute i and solutes j to n, respectively. n is total number of solutes present. Eqn (21) reduces to several well-known relationships as special cases. These include (1) the Langmuir equation for bisolute adsorption [37,41] ($b_{io} = b_{ij} = C_i = 1$). (2) the Jager and Erdos equation for a solute in a bisolute system [42] ($a_{io} = Y_i^*$, $b_{io} = a_{11} = b_{11} = b_{12} = 1$, $C_i = 0$), (3) the Radke and Prausnitz equation for single solutes [43], ($b_{11} = b_{10} - 1$, $c_1 = 1$), (4) the Freundlich equation for single solutes ($C_1 = 0$), and (5) the Langmuir equation for single solutes ($b_{10} = b_{11}$, $C_1 = 1$).

Using the general empirical Eqn (21) to characterize and calculate the adsorption equilibrium of organic solutes in dilute aqueous solutions, the adsorption capacity coefficient can be written as follows:

$$\bar{p}_i = [S_i C]/[S_i] = Y_i/X_i = f\,(X_i, X_j)_{a_{ij}, b_{ij}, c_i} = [C] K_{solvent,i} \qquad (22)$$

where $f\,(X_i, X_j)_{a_{ij}, b_{ij}, c_i}$ results from a parametric fit to the adsorption equilibria for multi-solute adsorption. Explicit expressions for f for single solute Langmuir and Freundlich expressions are given in reference [16]. At infinitely low bulk solute concentration $X_i, f_i = \bar{p}_i$ should be equal to Henry's constant, k_i^H for liquid phase adsorption.

Ideally, to characterize the extent of adsorption, $\bar{p}_i$ should be constant for a particular solute i. Failing this many workers have arbitrarily chosen some convenient X_i and (and $X_{j,o}$ initial values) to obtain a corresponding Y_i

from Eqn (22). For single solute adsorption $Y_{i=1}$ was chosen to represent $\bar{p}_{i=1}$ the capacity of a carbon and evaluated (1) at $X_i = 10^{-3}$M by McGuire et al [14]. (2) at X_1 = 1 mg/l by Dobbs et al. [44] to obtain a $_{10}$(or K_f in their nomenclature for the Freundlich coef.); (3) at fixed initial X_1=1000 mg/l with 5 g carbon by Giusti et al.[45] , and (4) when $b_{10} = b_{11} = 1$ and $a_{11} X_1 > c_1$ for the Langmuir equation, at $Y_1 = a_{10}/a_{11}$ by Martin and Al Bahrani [46-48]. Thus, in general from Eqns (15) and (22)

$$-RT \ln \bar{p}_i = \Delta G^{assoc}_{(solvent)} + \Theta \qquad (23)$$

where $\bar{p}_i$ = an adsorption capacity coefficient for solute i, $\Theta = RT \ln [C]$ is a constant for dilute solute adsorption and a given activated carbon column. With the requirement for dilute solute adsorption the complexity of solute-solute interaction in the adsorbed phase is bypassed.

Equation (9) can now be expressed in terms of the measurable adsorption capacity coefficient, $\bar{p}_i$ for comparison of different solutes as follows:

$$-RT \ln \bar{p}_i = K_1'' + \Delta G_{es,i} - K_2' \Delta A \qquad (24)$$

where $K_1'' = K_1' + \theta$, $K_2 = N\gamma$, as before, and $\Delta G_{es,i}$ is given in Appendix A. The subscript S_i is replaced by i.

DIFFUSIONAL KINETICS FOR ADSORPTION

Consider the case of radial diffusion into a sphere of radius R contained in a limited volume V of well-stirred bath solution (excluding the space occupied by the sphere) at initial concentration C_o of sorbate, and with the sphere initially free from solute. The diffusion equation is given by

$$\frac{\partial Q}{\partial t} = D_s \left(\frac{\partial^2 Q}{\partial r^2} + \frac{2}{r} \frac{\partial Q}{\partial r} \right) \qquad (25)$$

with boundary conditions

$$r = R;\ \rho_p D_s \frac{\partial Q}{\partial r} = -\frac{v}{s}\frac{\partial c}{\partial t} \tag{26}$$

$$r = 0;\ \frac{\partial Q}{\partial r} = 0 \tag{27}$$

with the Freundlich model

$$Q = K_f (C/C_o)^{n-1} \tag{28}$$

Suzuki and Kawazoe [49] have numerically solved Eqns (25) - (28) and presented the solutions in graphical form of C/C_o versus τ_s (where $\tau_s = D_s t/R^2$) for specific values of C_∞/C_o and n. They have also solved the equivalent pore diffusion problem using a Freundlich model with numerical solutions also presented in graphical form [50,51]. For the linear isotherm (n = 1) the analytical solution has been given by Crank [52].

MULTI-COMPONENT ADSORPTION

The Ideal Adsorbed Solution (IAS) theory approaches multicomponent adsorption as a classical thermodynamic phase equilibrium problem, equating the chemical potential of the ith species in the bulk solution to its chemical potential in the adsorbed phase. By assuming that the adsorbed phase forms an ideal solution [43], the following system of equations are obtained:

$$C_i(\pi, T, Z_i) = Z_i\, C_i^o\, (\pi, T) \tag{29}$$

$$\pi_i = \frac{RT}{A}\int_o^{C_i^o} \frac{Q_i}{C_i}\, dC_i^o \tag{30}$$

$$Q_i^o = f_i\, (C_i^o) \tag{31}$$

$$\pi_i = g_i\, (C_i^o) \tag{32}$$

$$\frac{1}{Q_T(\pi,T)} = \sum_{i=1}^{n} \frac{z_i}{Q_i^o(\pi,T)} \tag{33}$$

$$Z_i\, Q_T = Q_i \tag{34}$$

$$\sum_{i=1}^{n} Z_i = 1 \tag{35}$$

$$\pi_i = \pi_j = \pi \tag{36}$$

Note that this theory is not dependent on any particular form of the single solute isotherm. Once the dependence of Q_i^o on C_i^o is known, whether by an isotherm equation or from experimental data, the remaining equations may be solved.

Single Freundlich Equation

Single solute adsorption data may be expressed by the Freundlich equation:

$$Q_i = K_f\, C_i^{\,1/n} \tag{37}$$

Substituting this into Eqn (30) gives:

$$\pi_i = \frac{RT}{A} \int_o^{C_i^o} \frac{K_f C_i^{\,1/n}}{C_i}\, dC_i = \left(\frac{RT}{A}\right) n\, K_f C_i^{o\,1/n} \tag{38}$$

Instead of estimating A, the surface area of the interfacial region, the quantitiy(π_iA/RT) may be treated as one variable, since A remains constant. If the two Freundlich constants are known, π may be calculated directly from Eqn (38). The spreading pressure, π_i in the single solute system is a function of C_i^o, which in turn is a function of C_i and Z_i, from eqn (29). If all the C_i's are known, then the only unknown in Eqn (29) is Z_i, the mole fraction in the adsorbed phase. When the spreading pressures of the single solute systems at C_i^o are equal, along with the condition that ΣZ_i=1, then Z_i can be obtained directly. Finally q_T, and q_i may be calculated from Eqns (33) and (34).

Single Langmuir Equation

The IAS equations may also be solved with the Langmuir equation:

$$Q_i = \frac{Q^o b C_i}{1+bC_i} \tag{39}$$

and the equation corresponding to (30) becomes:

$$\pi_i = \frac{RT}{A} \int_0^{C_i^o} \frac{Q^o b C_i}{C_i(1+bC_i)}\, dC_i = \left(\frac{RT}{A}\right) Q^o \ln [1+bC_i] \tag{40}$$

Numerical Isotherm Equation

The accuracy with which experimental data are fit can be improved by fitting the Freudlich equation to sub-sections of the isotherm [38]. Extending this idea to the limit, a numerical representation of the single solute isotherm is obtained, with separate Freundlich constants representing the region in between any pair of data points. This model will be compared with the two models presented above.

Empirical Interpolation

Fritz and Schlünder [37] have proposed a method to fit their empirical Eqn (21) to dual-component adsorption data. In this case, Eqn (21) reduces to

$$Y_2 = \frac{a_{20}\, X_2^{b_{20}}}{X_2^{b_{22}} + a_{21}\, X_1^{b_{21}}} \tag{41}$$

with $a_{22} = 1$ and $a_2 = a_{20}$. If $b_2 \equiv b_{20} - b_{22}$ Eqn (41) can be inverted to give

$$\frac{X_2^{b_2+b_{22}}}{Y_2} = \frac{1}{a_2} X_2^{b_{22}} + \frac{a_{21}}{a_2} X_1^{b_{21}} \tag{42}$$

Remembering that for a pure single-solute adsorption isotherm

$$Y_2 = a_{20}\, X_2^{\,b_{20}-b_{22}} \equiv a_{20}\, X_2^{b_2} \tag{43}$$

where a_{20} (where $a_{20} \equiv K_f$) is the usual Freundlich preexponent and b_2 (where $b_2 \equiv n^{-1}$) is the usual Freundlich exponent. Thus, a_{20} and b_{22} are obtained from the pure isotherms. Assuming *$b_2 + b_{22} = 1$, and plotting X_2/Y_2 versus $X_c^{b_{22}}$ for different X_i values should give a linear plot with slope; a_2^{-1} and intercept $I_i = \frac{a_{21}}{a_2} X_i^{b_{21}}$ from Eqn (42). A plot of log $(a_2 I_i)$ versus log X_i obtains slope b_{21} and intercept log a_{21}. All the five parameters from Eqn (41) are thus obtained:

b_2, b_{22}, a_2, a_{21} and b_{21}.

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* The origin and validity of this assumption is neither discussed nor justified by Fritz and Schlunder [37].

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SECTION 6

RESULTS AND DISCUSSION

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In this section, the experimental batch adsorption isotherm results are presented and discussed. After discussing adsorption sensitivity and range of solution concentration used in this study, adsorption onto powdered activated carbon (PAC) is compared with adsorption onto graphitized carbon (GC). Kinetic studies are then discussed *ipso facto* and in connection with the time to reach pseudo-equilibrium and the effects of temperature. Thereafter both single and multi-component adsorption results are presented and analyzed with respect to the solvophobic thermodynamic ($c\phi$) approach.

SINGLE SOLUTE ADSORPTION SENSITIVITY

In this section we present results indicating the sensitivity of the Langmuirian parameters as a function of aqueous solute concentration range. Typical primary data for the adsorption of 2-pentyl phenol on powdered activated carbon (PAC) Filtrasorb-400 are dipicted in Fig. 4a for the complete range of aqueous solute concentrations from 0.33 to 26.29 mg/l, and in Fig. 4b for the low concentration range from 0.20 to 1.08 mg/l. Similar data for other members of the alkyl phenol homologous series are summarized with their fitted Langmuirian parameters in Table 3.

Although the fits as measured by the correlation coefficient, r, appear to be relatively good and do not significantly differ between the two sets of data, the Langmuirian parameters do differ significantly, emphasizing the importance of obtaining a wide range of data of several orders of magnitude. As a result, adsorption data for as wide a range as technically possible was measured in this study.

COMPARISON BETWEEN POWDERED ACTIVATED CARBON AND GRAPHITIZED CARBON

A series of alkyl phenols was used to compare the aqueous phase adsorption between a highly porous powdered activated carbon (PAC) with a surfacearea of about 1013 m^2/g and a non-porous graphitized carbon (GC) with a surface area of about 89 m^2/g. Typical Freundlich adsorption isotherms for the alkyl-phenols are shown for 4-ethyl phenol in Fig. 5, where it can be seen that favorable adsorption (large n) is obtained with the PAC while

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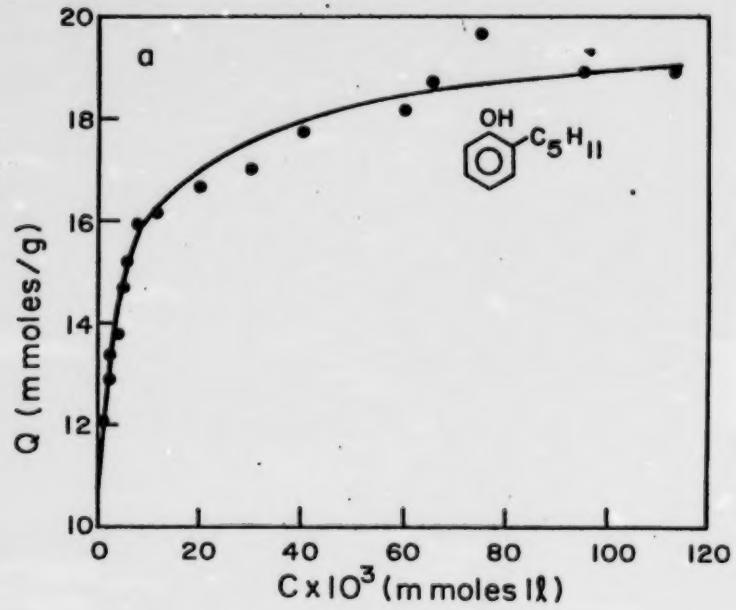

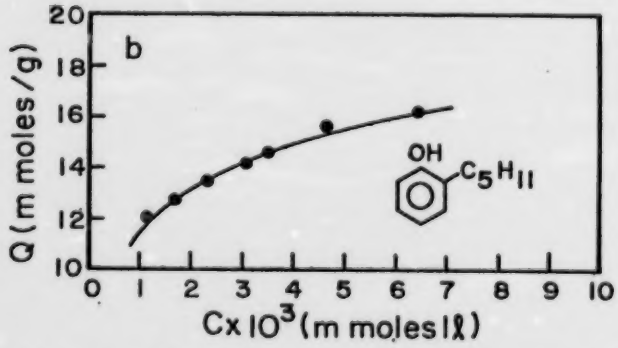

Fig. 4. Typical primary adsorption data for (a) the complete, and (b) the low concentration range for 2-pentyl phenol.

TABLE 3. ADSORPTION ISOTHERM MEASUREMENTS FITTED TO THE LANGMUIRIAN MODEL FOR ALKYL PHENOLS*

Solute	Molecular weight	LOW CONCENTRATION RANGE					COMPLETE CONCENTRATION RANGE				
		Conc. range mg/ℓ	# of pts.	Q^o mmole/g	$\ell n(Q^o b)$ ---	Correl,r ---	Conc. range mg/ℓ	# of pts.	Q^o mmole/g	$\ell n(Q^o b)$ ---	Correl,r
phenol	94.11	0.32 -1.17	6	0.33(3)	2.2(0)	0.92(0)	0.38-12.42	11	0.73(8)	4.7(3)	0.93(4)
2-cresol	108.14	0.65 - 2.83	6	0.55(0)	2.5(3)	0.97(2)	0.65-18.81	10	1.03(5)	5.4(0)	0.96(7)
4-ethyl phenol	122.16	0.31 - 1.35	---	0.79(4)	3.0(1)	0.93(9)	0.24-24.68	9	1.44(5)	5.9(5)	0.93(2)
4-propyl phenol	136.19	0.10 - 1.93	4	1.01(3)	2.7(4)	0.97(7)	0.68-25.74	10	1.62(2)	6.3(2)	0.95(8)
2-butyl phenol	150.22	0.26 - 0.96	5	0.91(2)	4.1(2)	0.99(1)	0.30-22.38	6	1.70(2)	7.2(6)	0.9[illegible](6)
2-pentyl phenol	164.25	0.20 - 1.08	7	1.1(5)	4.2(8)	0.97(9)	0.33-26.29	16	1.78(3)	7.2(6)	0.94(1)

* $Q = \frac{Q^o b C}{1 + b C}$, where a) $bC \gg 1$, $Q \to Q^o$, saturated adsorption, and b) $BC \ll 1$, $Q/C \to Q^o b$, Henry's Constant

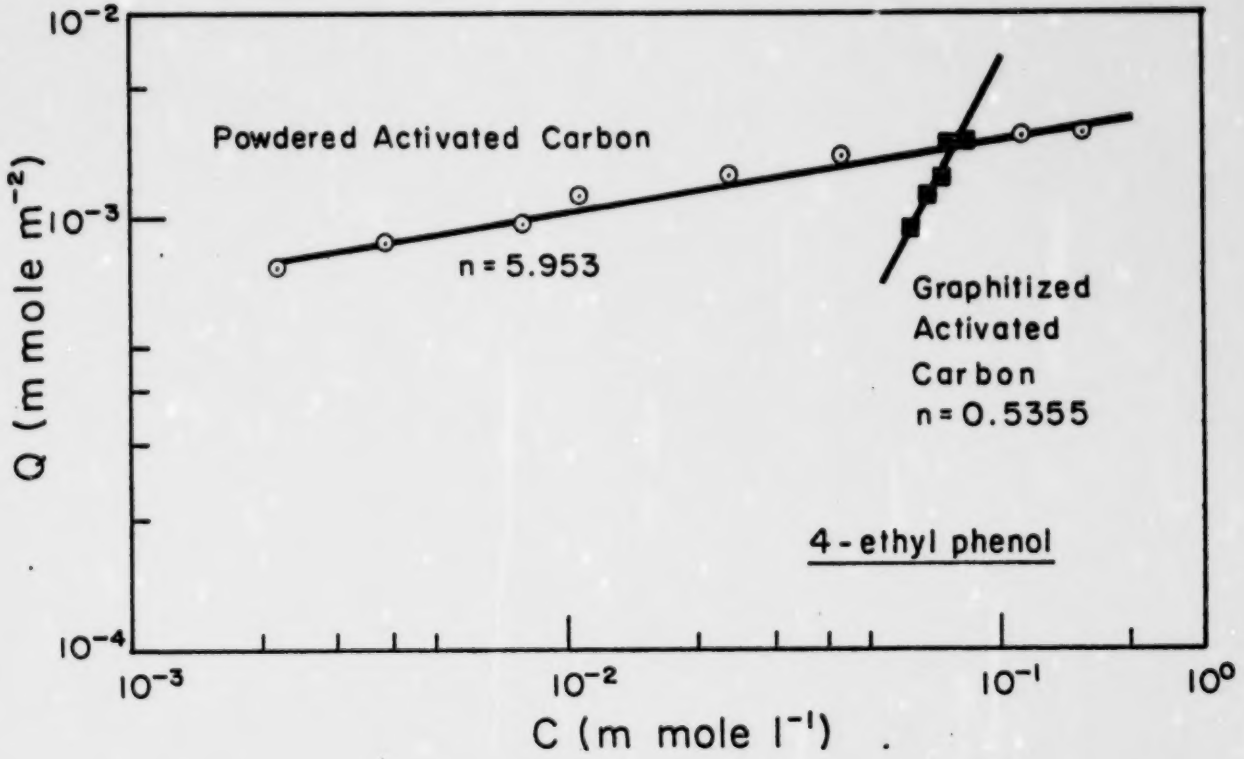

Fig. 5. Adsorption of 4-ethyl phenol on powdered activated carbon and graphitized activated carbon.

unfavorable adsorption (small n) is obtained with the GC. For convenience such that the two plots appear in the same range, the Q-values are normalized by sorbent surface area rather than by the usual weight of sorbent.

The adsorption data for five members of the alkly phenol homologous series is summarized in terms of Freundlich parameters in Table 4 together with the cavity surface area of each solute. The value n obtained from the Freundlich model is considered a rough indicator of adsorption intensity, and is plotted in Fig. 6 against cavity surface area for each solute. Besides phenol, the n-values increase with ascending order of the series for both adsorbents; the slope is 9.61 times greater for the graphitized carbon than for the powdered activated carbon (PAC). The absolute values, however, are much larger for the activated surface than for the graphitized surface. This sugg[illegible] that the activated surface is more compatible for adsorbing the more polar molecules of the homologous series. Edge effects, oxide, hydroxyl and other polar or charged moeities on the activated surface probably play an important role in this effect.

KINETIC STUDIES

The time to reach a plateau or pseudo-equilibrium adsorption capacity for the alkyl phenols on PAC is summarized in Table 5. Pseudo-equilibrium because there appears to be a fast adsorption phase of the order of hours and days to reach the pseudo-equilibrium plateau and a slow adsorption phase of the order of weeks to reach final equilibrium.

The pseudo-plateau time and equilibrium was used for all the adsorption work. Note how both the time and equilibrium values increase with molecular weight right up to hexyl phenol. This increase is reconfirmed in the pseudo equilibrium studies reported below.*

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* "Pseudo" will be dropped from now on although it still applies to the short-term adsorption equilibrium.

TABLE 4. ADSORPTION ON POWDERED ACTIVATED CARBON AND GRAPHITIZED CARBON

Compound	Mol. wt.	# of data pts.	Freundlich parameters			Cavity surface area, TSA Å^2
			K_f mmole m^{-2}	n ---	r ---	
I GRAPHITE (89 m^2/g)						
phenol	94.1	7	3.5 x 10^{28}	0.03(7)	0.84(2)	249.1
2-cresol	108.1	7	3193	0.14(8)	0.81(9)	274.3
4-ethyl phenol	122.1	5	0.1651	0.53(5)	0.96(7)	306.3
4n-propyl phenol	136.2	6	5.088	0.35(8)	0.90(5)	336.8
2-butyl phenol	150.2	8	0.0223	1.39(9)	0.85(5)	363.1
II PAC (1013 m^2/g)						
phenol	94.1	11	1.0616×10^{-3}	6.42(2)	0.51(6)	249.1
2-cresol	108.1	10	1.616×10^{-3}	5.33(5)	0.97(4)	274.3
4-ethyl phenol	122.1	9	2.211×10^{-3}	6.02(1)	0.94(6)	306.3
4n-propyl phenol	136.2	7	2.2891×10^{-3}	6.64(5)	0.97(3)	336.8
2-butyl phenol	150.2	10	2.655×10^{-3}	6.72(6)	0.97(9)	363.1

* Obtained from a plot of log q versus loc C, where q has units mmoles adsorbed per m^2 of adsorbent surface area and C has units mmoles ℓ^{-1}.

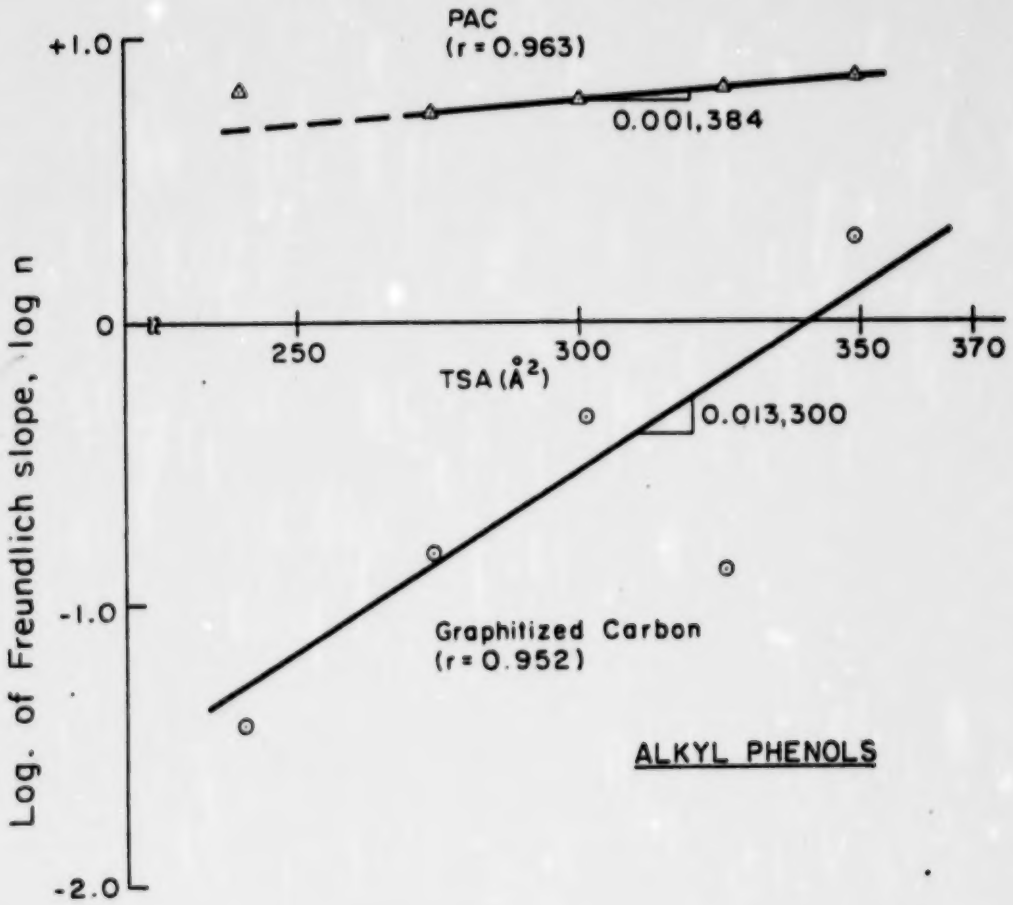

Fig. 6. Logarithm of the Freundlich slope, log n, versus total cavity surface area, TSA, for powdered activated carbon and graphitized carbon.

TABLE 5. ADSORPTION KINETICS OF ALKYL PHENOLS ON PAC

Solute	Molecular weight	C_o* mmole/ℓ	Q_∞† mmole/ℓ	t_∞† hr
phenol	94.1	0.14(5)	0.64(9)	1.0
2-cresol	108.2	0.11(4)	0.73(7)	4.0
2-ethyl phenol	122.3	0.08(2)	0.70(8)	8.0
4n-propyl phenol	136.4	---	0.90(9)	9.0
2-butyl phenol	150.2	0.12(5)	1.06(8)	11.0
2-pentyl phenol	164.3	0.09(0)	1.08(3)	12.0
2-hexyl phenol	178.4	0.14(0)	1.28(6)	14.0

* Initial concentration before adding the PAC

† Time to reach pseudo-equilibrium, t_∞, resulting in maximum adsorption Q_∞.

Surface and Pore Diffusion Coefficients

Plots, showing the experimental data points superimposed onto the theoretical curves based on the Freundlich model obtained from Suzuki and Kawazoe [49], are presented in Figs 7a and 7b for the surface and pore diffusion models. The detailed procedure to obtain D_s and D_e is given in references [49-51] and involves the superposition of an experimental C/C_o versus t onto a theoretical curve of known C_∞/C_o and Freundlich parameter, n *. Comparison of the horizontal axis gives the theoretical τ_s at a chosen experimental t (secs). From an estimate of the average particle radius, $R \approx 27.75 \times 10^{-4}$ cm the surface diffusion coefficient is estimated from $D_s = R^2\tau_s/t$, while the pore diffusion coefficient $D_e = \tau R^2 \rho_p (1000) k_f/(60tC_o)$ requires the Freundlich parameter k_f, the particle density (dry) ρ_p and the initial feed concentration C_o.

The results obtained from this procedure are summarized in Table 6. The surface and pore diffusion coefficients for 4n-propyl phenol are unexplainably too low. The rest of the results follow the expected trend of decreased diffusion rate with increased solute cavity surface area (TSA) as shown in Table 7.

Since $D_e \approx D_b$, the D_e values are within an acceptable range of values, and the D_s values are comparable to previously reported values in the literature. For example using a single parameter approach Van Vliet et al [53] report $D_s = 1.24 \times 10^{-9}$ cm^2 sec^{-1} for phenol in Filtrasorb 400, while Peel et al [54] report $D_s \approx 7.75$ to 9.01×10^{-8} cm^2 sec^{-1} for rapid diffusion in the macropores of Filtrasorb 400 using their branched pore kinetic model.

Temperature Effects

2-butyl phenol was sorbed onto PAC at four different temperatures, 20, 30, 40 and 50°C to determine the effect of temperature on the adsorption dynamics. Using both the single parameter surface and pore diffusion models to fit the experimental data, $D_s(t)$ and $D_e(t)$ were obtained and plotted in

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* Note that both the theoretical and experimental axes are drawn to the same scale.

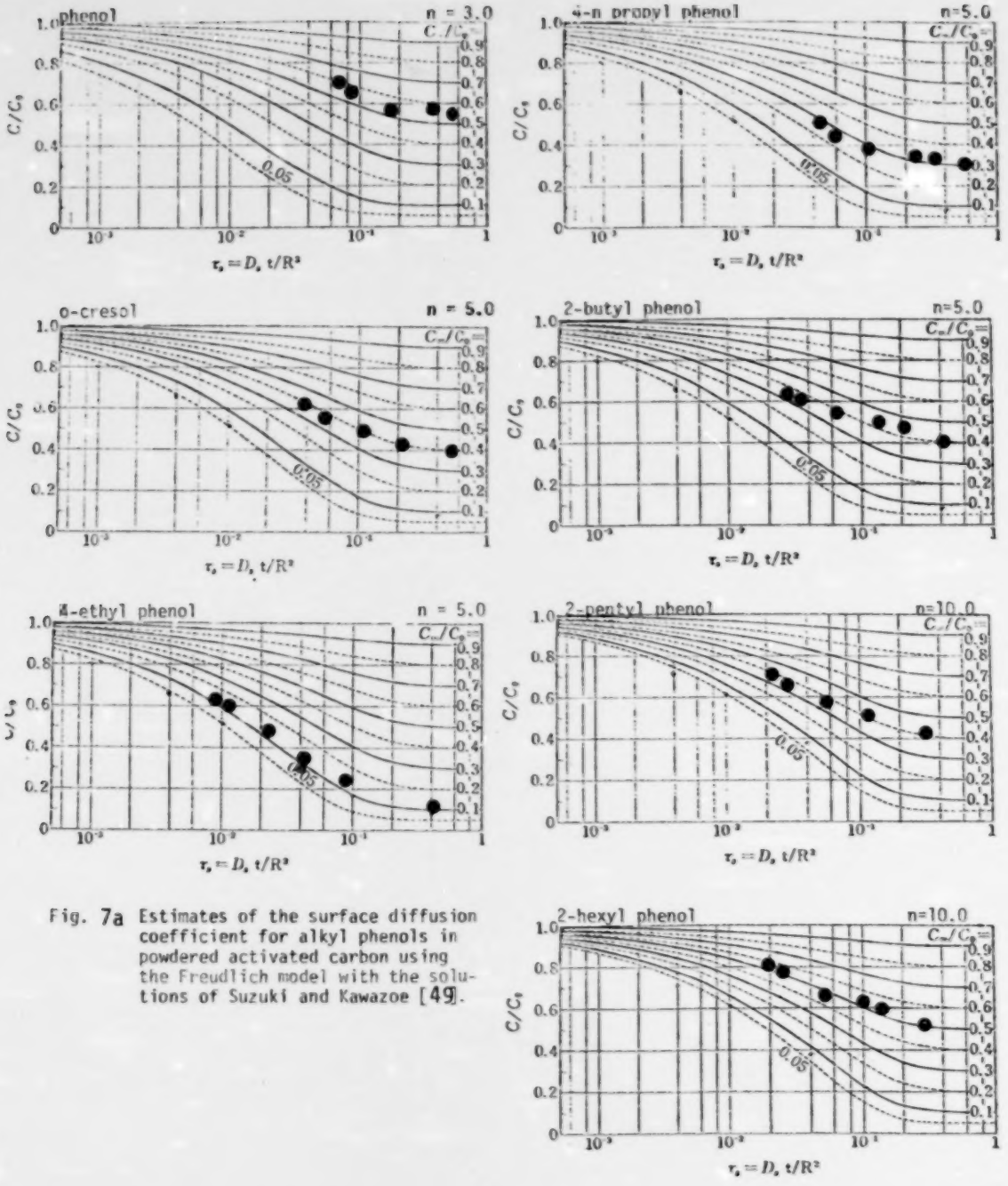

Fig. 7a Estimates of the surface diffusion coefficient for alkyl phenols in powdered activated carbon using the Freudlich model with the solutions of Suzuki and Kawazoe [49].

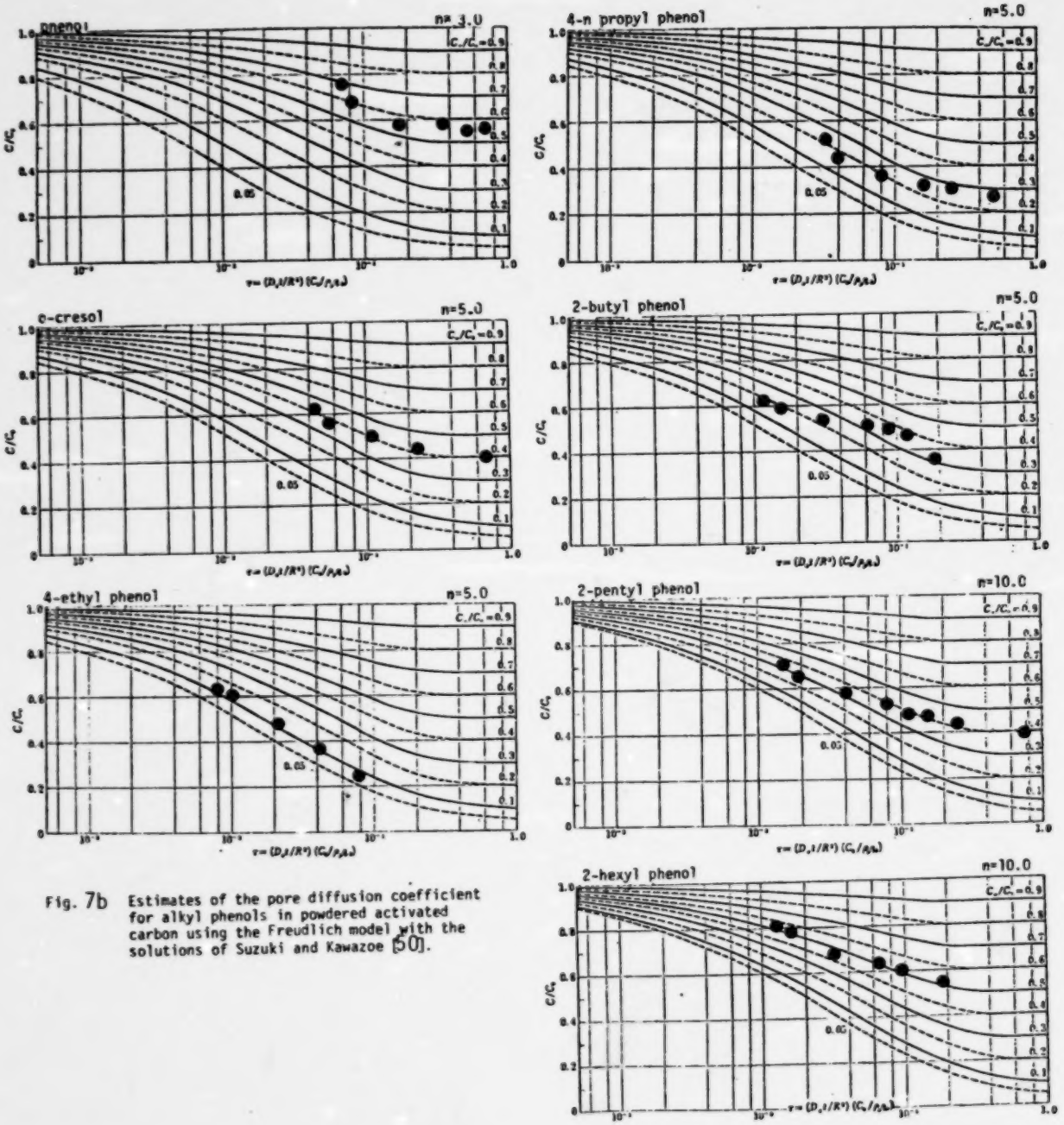

Fig. 7b Estimates of the pore diffusion coefficient for alkyl phenols in powdered activated carbon using the Freudlich model with the solutions of Suzuki and Kawazoe [50].

TABLE 6. SURFACE AND PORE DIFFUSION COEFFICIENTS OBTAINED FROM ADSORPTION KINETICS

Solute	Molecular weight	Diffusion coefficients, x 10^6		
		Bulk* D_b $cm^2\ sec^{-1}$	Surface† D_s $cm^2\ sec^{-1}$	Pore‡ D_e $cm^2\ sec^{-1}$
1. phenol	94.1	9.127	5.26×10^{-4}	8.88
2. 2-cresol	108.2	8.122	4.62×10^{-4}	8.15
3. 4-n-propyl phenol	122.3	7.366	1.28×10^{-4}	2.16
4. 4-ethyl phenol	136.4	6.773	4.36×10^{-4}	8.09
5. 2-butyl phenol	150.2	6.292	3.59×10^{-4}	6.97
6. 2-pentyl phenol	164.3	5.893	3.21×10^{-4}	6.62
7. 2-hexyl phenol	178.4	5.520	2.695×10^{-4}	5.56

* For comparison, the bulk or external binary diffusion coefficients are estimated from Ref.[64], pp 267 and pp 58 from $D^\circ = 7.4 \times 10^{-8} (\phi M_B)^{1/2} T/\eta_B V_A^{0.6}$, where T = 293°K, η_B(water at 20°C) = 1.0005 cp, ϕ = association factor for water $\phi = 2.6$, $M_B = 18$(water), and the molar volumes V_A we estimated from LeBas' additive volume increments. For the seven components above, V_A's are 103.4, 125.6, 47.8, 170.0, 192.2, 214.4, and 236.6cm^3/g-mole, respectively.

† For model see Ref.[49] and text, where $D_s = \tau_s R^2/t$, R is the mean particle radius, = 27.75×10^{-4} cm (see Table I).

‡ For model see Ref. [50] and text, where $D_e = \tau R^2 \rho_p (1000) K_f/(60\ t\ 60)$, where K_f is the Freundlich preexponent (mmoles/g), ρ_p is the particle density on a water-free basis (gm/cm^3), and $C = C_o$ at $t = 0$. The (q_o, C_o) pairs for each of the seven solutes were (0.4198, 0.145); (0.3978, 0.114); (0.289, 0.082), (0.558, 0.123); (0.947, 0.125); (0.508, 0.0896); and (0.4850, 0.1398), respectively.

TABLE 7. LINEAR CORRELATION OF DIFFUSION COEFFICIENTS WITH SOLUTE CAVITY SURFACE AREA (TSA)

Diffusion coefficient $cm^2\ sec^{-1}$	Intercept	Slope	Corr. Coef. r
D_b	14.450	-0.023	0.99(2)
D_s^*	9.070	-0.016	0.99(7)
D_e^*	13.659	-0.019	0.94(4)

* Except for 4n-propyl phenol value

an Arrhenius plot to obtain the activation energy, E_a. From the plots, shown in Fig. 8, E_a values equal to -2.79 cal gmole^{-1} and -3.20 cal gmole^{-1} were obtained for surface and pore diffusion, respectively. Two competing phenomena are probably occurring simultaneously. While film mass transfer and internal diffusion are expected to increase with temperature, the reverse is true for exothermic reactions such as for the adsorption of organics onto PAC. The linear plots in Fig. 8 and the small negative activation energies that result, highlight both the competition and the relative importance of the exothermic adsorption reaction.

SINGLE SOLUTE ADSORPTION

The major experimental effort of this study involved the careful measurement and accumulation of statistically relevant data of single solute aqueous phase adsorption isotherms of two homologous series. The main purpose for doing this is to establish a reliable data-base for evaluating the efficacy of the solvophobic thermodynamic treatment in ranking the adsorption intensity of the different members of different homologous series. Homologous series of alkyl phenols and aliphatic alcohols were chosen to represent aromatic and aliphatic organic groups in water, respectively.

Alkyl Phenols

The raw data for the adsorption isotherms are recorded in Appendix 1 of reference [55]. The data are expressed in tabular form, and are fitted to the Langmuir isotherm model. The raw data for each compound are plotted, Q in mmole/g and C in mmole/L. These data clearly exhibit the Langmuirian isotherm form. The linearized Langmuir model is plotted as 1/Q versus 1/C. The kinetics for each compound were evaluated, and 24 hours was found to be sufficient to attain pseudo equilibrium for each case.

The 19 alkyl phenols studied and their adsorption capacities on Filtrasorb-400 PAC are summarized in Table 8. Nine compounds studied were phenols with a linear alkyl side-chain of increasing length. The first compound, phenol, has no alkyl group associated with it, while 2-pentyl phenol has a

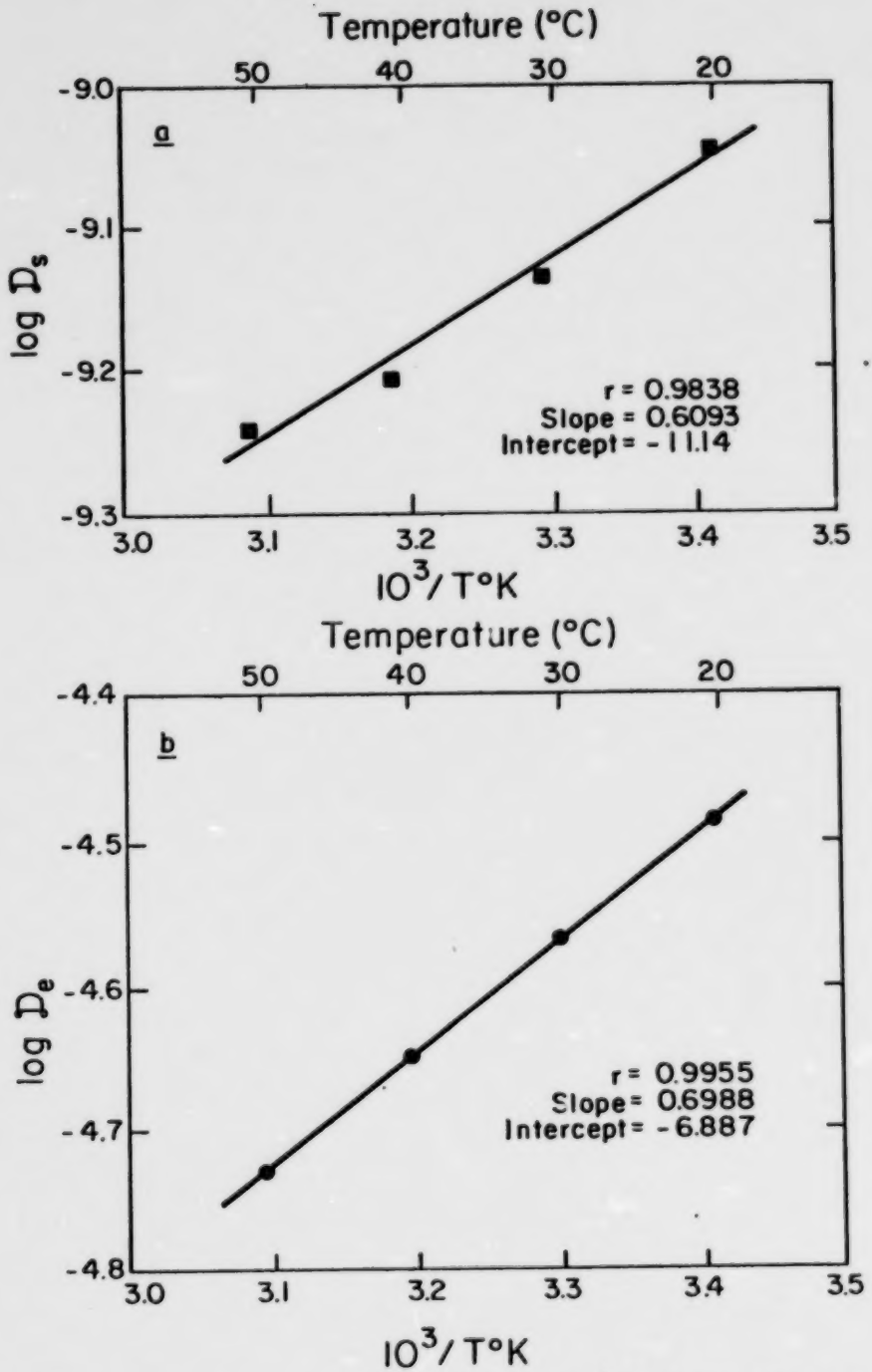

Fig. 8 Arrhenius plots for (a) surface diffusivity, and (b) pore diffusivity during adsorption of 2-butyl phenol.

TABLE 8. ADSORPTION ISOTHERM MEASUREMENTS FITTED TO THE LANGMUIRIAN MODEL FOR ALKYL PHENOLS

Solute	MW	TSA* ($Å^2$)	Concentration Range (mmole/L)	No. or Points	Q^o (mmole/g)	b $(mmole/L)^{-1}$	ln Q^o (mmole/g)	ln $Q^o b$+	r
1. Phenol	94.1	249.1	.132 - .004	11	0.73(8)	150.4	-0.30(4)	4.7(3)	0.93(4)
2. 2-methl Phenol	108.1	274.3	.174 - .006	10	1.03(5)	213.7	0.03(4)	5.4(0)	0.96(7)
3. 4-ethyl Phenol	122.2	306.3	.202 - .002	9	1.44(5)	266.6	0.36(8)	5.9(5)	0.93(2)
4. 2,6-dimethyl phenol	122.2	296.3	.171 - .006	8	2.27(1)	308.7	0.82(0)	6.5(5)	0.93(5)
5. 2,3-dimethyl phenol	122.2	295.3	.140 - .012	11	1.79(5)	282.4	0.58(5)	6.2(3)	0.97(5)
6. 3,4-dimethyl phenol	122.2	297.9	.158 - .005	10	1.81(3)	266.4	0.59(7)	6.1(8)	0.95(2)
7. 3,5-dimethyl phenol	122.2	306.1	.188 - .007	9	1.61(7)	299.7	0.48(1)	6.1(8)	0.96(4)
8. 2,5-dimethyl phenol	122.2	302.8	.136 - .008	9	1.92(1)	238.2	0.65(3)	6.1(3)	0.98(0)
9. 4-propyl phenol	136.2	336.8	.189 - .005	7	1.62(2)	343.6	0.48(4)	6.3(2)	0.95(8)
10. 4-isopropyl	136.2	321.7	.145 - .011	6	3.77(3)	92.4	1.32(8)	5.8(5)	0.95(8)
11. 2,3,5-trimethyl phl.	136.2	323.5	.230 - .004	11	2.27(2)	302.9	0.82(1)	6.5(3)	0.93(4)
12. 2,3,6-trimethyl phl.	136.2	317.3	.194 - .006	10	2.45(2)	335.0	0.89(7)	6.7(1)	0.92(7)
13. 2-butyl phenol	150.2	363.1	.149 - .002	6	1.70(2)	833.1	0.53(2)	7.2(6)	0.95(6)
14. 4-butyl phenol	150.2	366.9	.057 - .011	6	2.26(5)	613.3	0.81(8)	7.23(7)	0.62(9)[a]
15. 4-tert butyl phenol	150.2	345.1	.133 - .008	8	1.53(9)	473.5	0.43(1)	6.5(9)	0.93(2)
16. 2-pentyl phenol	164.3	394.0	.160 - .002	16	1.78(3)	800.9	0.57(8)	7.2(6)	0.94(1)
17. 4-pentyl phenol	164.3	397.4	.127 - .004	10	2.56(3)	672.3	0.94(1)	7.4(5)	0.89(4)
18. 4-tert pentyl phenol	164.3	362.3	.138 - .015	7	4.93(5)	177.4	1.59(6)	6.7(8)	0.93(3)
19. 2-hexyl phenol	178.3	423.7	.163 - .001	6	1.79(4)	733.3	0.58(4)	7.1(8)	0.91(9)

* Total cavity surface areas (TSA) calculated using the MSD Program [56]

\+ Experimental error for one standard deviation is about ± 0.10 units for ln $Q^o b$

a difficult to dissolve

linear 5-carbon alkyl side chain. Seven compounds studied were phenols with the alkyl side-chains in various positions. The other three compounds studied were branched isomers of the linear set.

Linear

In Fig. 9, the linear alkyl phenols are fitted to the linearized form of the Langmuir model. The slope of the best fit line, $1/Q^{o}b$, is a measure of the adsorption capacity for each compound. $Q^{o}b$ is Henry's constant, i.e., the slope of Q versus C at infinite dilution. As the concentration, C, of the solute goes to zero, so Q, the amount adsorbed per mass of carbon, divided by C goes to $Q^{o}b$. The lower the slope in Fig. 9, the greater the adsorption. As the length of the alkyl chain increases, adsorption is seen to increase, as expected. The phenol molecule is somewhat polar, with its hydroxyl group attracted to the solvent molecules via hydrogen bonding. As the alkyl groups are introduced, however, the molecule offers an increasingly non-polar surface for adsorption to the non-polar carbon sorbent. The longer the alkyl side-chain, the more surface area is available for attachment to the carbon, hence the greater adsorption.

In Table 9, the Langmuir adsorption parameters Q^{o}, $\ln Q^{o}$ and $\ln Q^{o}b$ are correlated for the eight alkyl phenols with molecular weight. Very good correlations are obtained, as expected. Although the correlation coefficient for each parameter with molecular weight is significantly greater than zero (95% confidence), the values, however, are not significantly different from one another (95% confidence).

In order to test the simplified version of the solvophobic theory, the molecular cavity surface area of each solute (i.e. the total surface area, TSA) was calculated using the MSD program [56]. The TSA for each alkyl phenol is then correlated with the Langmuir adsorption parameters in an attempt to verify the theory [Eqn (24)] as a predictive measure of solute adsorption. In Table 9, we observe the adsorptivities for the linear alkyl phenols also correlate well with TSA. However, TSA, does not significantly correlate with adsorption parameters any better than molecular weight for the linear alkyl phenols at this level of confidence (95%) and for these few sample pairs (six)

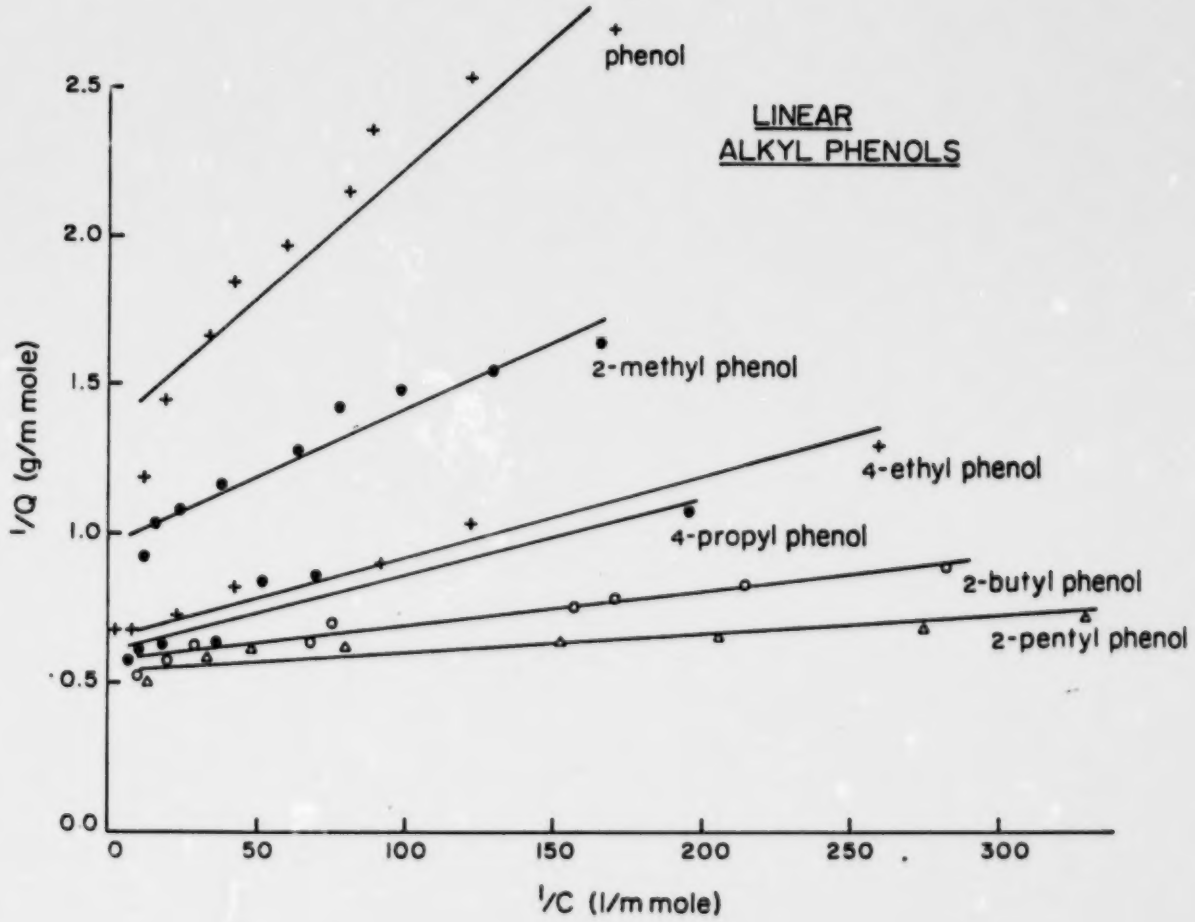

Fig. 9 Langmuir adsorption data for linear alkyl phenols.

TABLE 9. CORRELATION COEFFICIENT r FOR LANGMUIRIAN ADSORPTION PARAMETERS VS. MOLECULAR WEIGHT AND TOTAL SURFACE AREA FOR THE ALKYL PHENOLS

Adsorption Parameter	Linear Alkyl Phenols*		Linear and Non-Linear Alkyl Phenols X		Linear and Non-linear and Fragmented Alkyl Phenols†		Singer and Yen‡	
	Molecular Weight	TSA $A^{\circ 2}$	Molecular Weight	TSA $A^{\circ 2}$	Molecular Weight	TSA $A^{\circ 2}$	Molecular Weight	TSA $A^{\circ 2}$
Q^o	0.89(7)	0.90(7)	0.57(6)	0.43(5)	0.56(5)	0.42(3)	0.98(2)	0.99(8)
$\ln Q^o$	0.92(7)	0.93(2)	0.73(2)	0.62(7)	0.65(1)	0.53(1)	0.96(6)	0.98(9)
$\ln Q^o b$	0.98(3)	0.98(2)	0.93(7)	0.97(5)	0.88(7)	0.90(0)	0.95(5)	0.98(2)

* Compounds 1-3, 9, 13, 14, 16, 17, Table 8

X Compounds 1-3, 9, 10,13,14, 15, 16, 17, 18, Table 8

† Compounds 1-18, Table 8

‡ Compounds 1-4, 9, Table 8 Adsorption on PX-21 PAC from Ref [19]

Since the cϕ-theory was developed to account for branching and other structural changes, these results are expected.

Non-linear fragmented or position isomers.

Due to the difficulty in obtaining true non-linear (branched) isomers of the attached linear-alkyl groups, a set of fragmented isomers (i.e., the alkyl group is distributed around the phenol ring in methyl fragments while maintaining constant molecular weight) were tested. These solutes are numbered 4 through 8, 11 and 12 in Table 8. Contrary to the usual decrease in adsorption capacity resulting from branching, the fragmented compounds exhibit increased values over the linear compounds (Fig. 10). The adsorption parameter $\ln Q^{o}b$ is plotted against molecular weight and TSA in Figs. 10 and 11 where it can be seen that the correlation coefficient is slightly higher for molecular weight than TSA. Clearly the simplified cϕ-theory is no better (at 95% confidence level) than molecular weight for these 19 compounds.

These results together with less comprehensive adsorption data on PX-21 activated carbon from Singer and Yen are correlated with molecular weight and TSA in Table 9. TSA correlates well with all three adsorption parameters. The correlation coefficients with molecular weight are not as good as with TSA. Again, due to the limited number of compounds, the correlation coefficients are not statistically significantly different from each other.

To interpret these results two effects are proposed here. The addition of one or more substituents on the phenol ring affect the π-electron distribution of the molecule. This in turn should influence interactions with the solvent and the sorbent. Thus, the more comprehensive cϕ-model is needed to describe these association adsorption processes. A second and complementary effect has to do with the geometric configuration of the sorbate during adsorption. With one substituent alkyl group, it is likely that the non-polar alkyl group is oriented toward the non-polar adsorbent surface with the phenol ring and its π-electrons oriented toward the polar solvent (i.e., end-on attachment). When several alkyl substituents are attached to the phenol ring, all the non-polar groups are "squeezed-out" of the polar solvent and drawn toward the non-polar sorbent causing the phenol ring to "hug" this surface (i.e., parallel attachment). This should result in an increased adsorption capacity for the fragmented alkyl isomers as shown in Table 8 and Fig. 11.

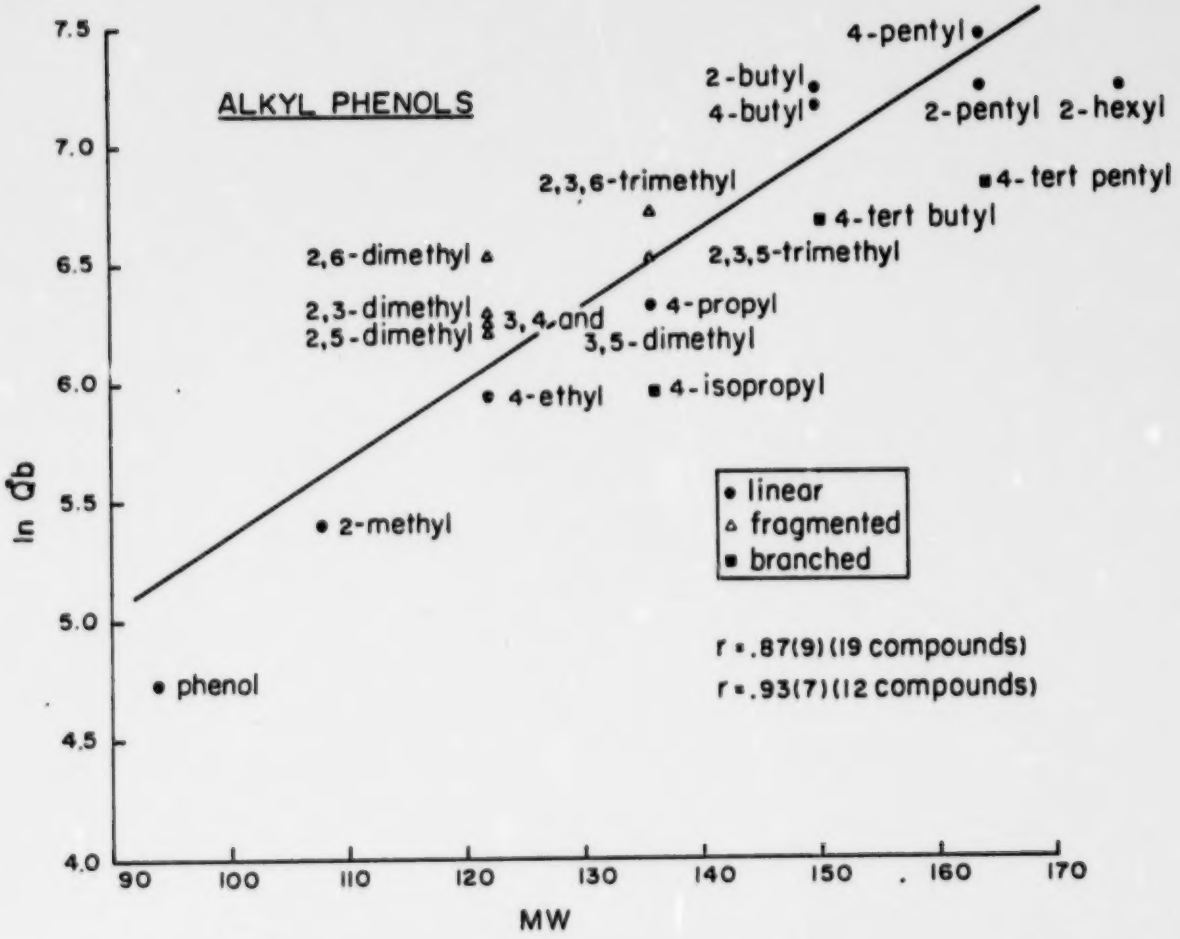

Fig. 10. Adsorption capacity ($\ell nQ^{o}b$) versus MW for linear and non-linear fragmented phenols. Except for the phenol data point, all the symbols describe the position and type of alkyl group attached to phenol. See Table 8 for details.

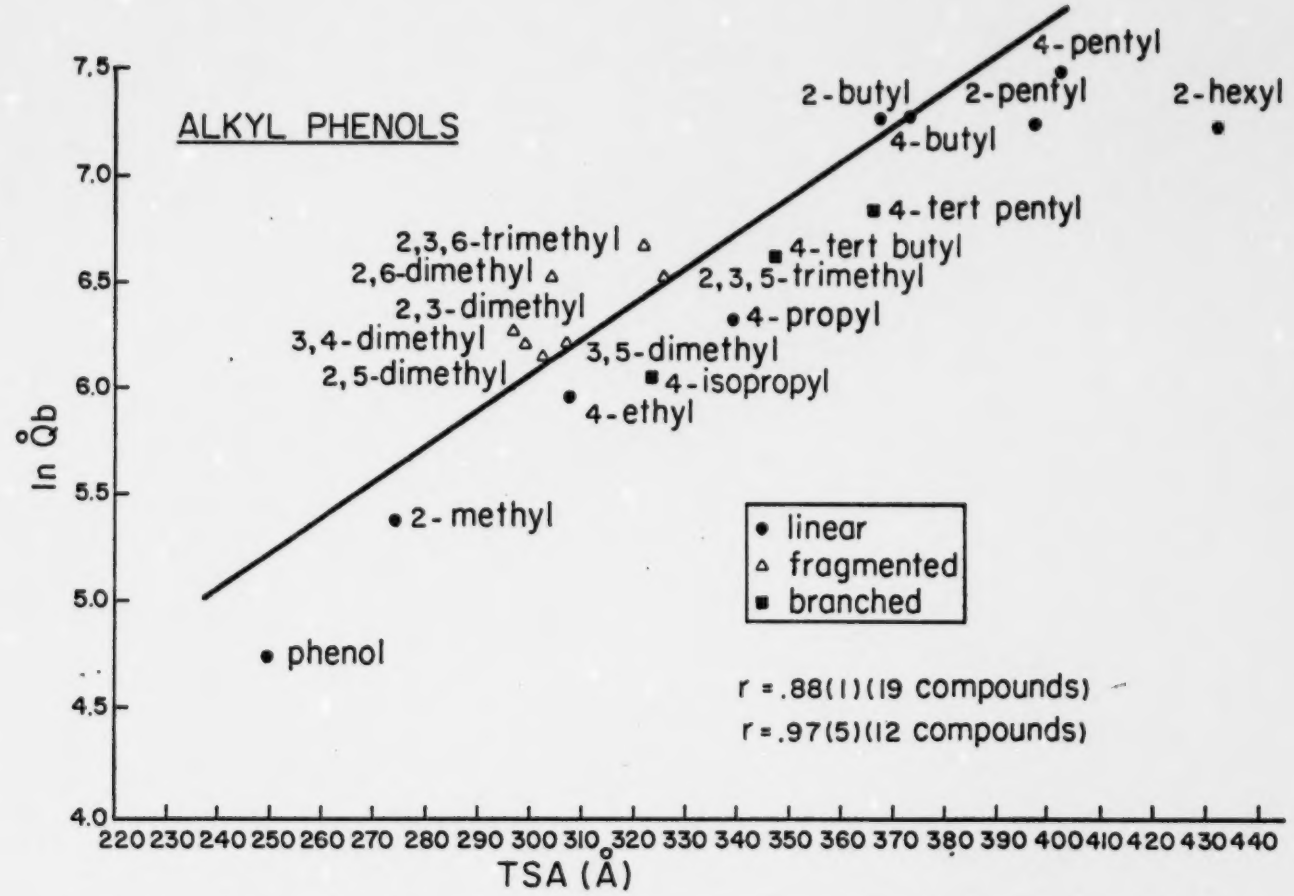

Fig. 11. Adsorption capacity ($\ell n Q^{o}b$) versus cavity surface area for linear and non-linear fragmented alkyl phenols.

The effect is further illustrated in Fig. 12. If the adsorption of each of the three alkyl phenols (MW=136.2) was a function of molecular weight alone, the data points for each compound should fall along a common line. This is not the case. Both 2,3,5-and 2,3,6- trimethyl phenol have smaller total surface areas than 4-propyl phenol, however, because of the orientation arguments above exibit higher adsorption capacity.

It is interesting to note the adsorption of 2,3,6-trimethyl phenol is somewhat greater than 2,3,5-trimethyl phenol in terms of both Q^o and Q^ob. The presence of a non-polar methyl group on each side of the hydroxyl group may sterically hinder the ability of the hydroxyl group to hydrogen-bond with the aqueous solvent. This would result in an increase in adsorption.

Q^o and $\ln Q^o$ are also correlated with molecular weight and TSA for each solute as shown in Table 9. Neither adsorption parameter correlates well with either solute characteristic for linear and fragmented compounds.

Q^o is a measure of the total amount of solute the carbon can adsorb at saturation. This parameter is commonly employed in water and wastewater treatment as a measure to characterize a compound's ability to adsorb to a specific activated carbon. Q^o does not really lend itself, however, to the solvophobic theory treatment. The theory is postulated to describe adsorption in dilute aqueous solutions. This is the region characterized by Henry's Law, i.e., at infinite dilution, when the solute adsorption approaches zero. It is this region of the isotherm which is characterized by the parameter Q^ob. At low solute concentration the solute molecules are assumed not to interfere or interact with one another. They are, in effect, unaware of each others' presence. At saturation however, this assumption is probably no longer valid, and solute-solute effects should be considered.

It is suprising the correlation of Q^o with TSA is so low, considering the strong correlation between the two when only the linear alkyl phenols are considered.

A word of caution is needed regarding the experimental results presented in Table 9. Because of experimental error, it is extremely difficult to distinquish the difference in adsorption capacity ($\ln Q^ob$) between fragmented isomers of the same molecular weight (see solutes 4-8, 11,12, and footnote † in Table 8).

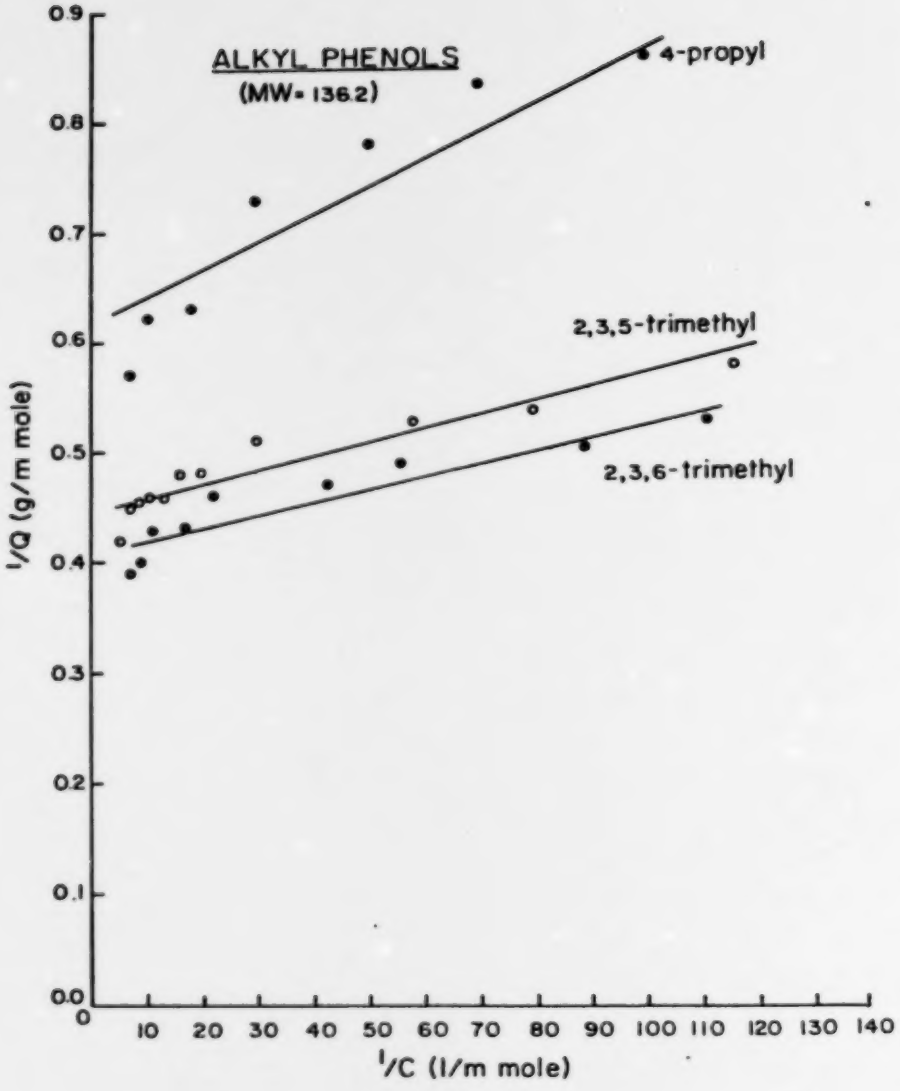

Fig. 12. Langmuir adsorption data for alkyl phenols with MW = 136.2.

Dissociation effects

Zogorski and Faust [57] have shown that inorganic ions (phosphate buffer) do not affect the adsorption of the undissociated form of several halogenated phenol adsorbates. Adsorption of the anionic form of the compounds, however, is increased in the presence of these ions, possibly through reduction of the repulsive forces between adsorbed molecules and the carbon surface, or between anions adsorbed at the surface. If a large percentage of the solute molecules were present in the dissociated form, the inclusion of phosphate buffer in our procedure may have influenced adsorption considerably, affecting the correlations with TSA.

Of the nineteen alkyl phenols studied, phenol has the greatest tendency to dissociate. It has a dissociation constant $K_A = 1.2 \times 10^{-10}$ [58]. At pH = 7, less than one percent of phenol exists in the anionic form in aqueous solution [59]. Subsequently, we can assume our equilibrium adsorption parameters are characteristic of the undissociated molecular species.

It was our intention to minimize error by controlling as many variables as possible in the experimental procedure. This included in particular keeping temperature ($T = 20 \pm 0.5°C$) and pH ($pH = 7.0 \pm 0.1$) constant.

Alcohols

The raw data for the adsorption isotherms are recorded in appendix 1 of reference [55]. The data are expressed in tabular form, and are fitted to the Langmuir isotherm model. The raw data for each compound are plotted, Q in mmole/g and C in mmole/L. These data clearly exhibit the Languirian isotherm form. The linearized Languir model is plotted as 1/Q versus 1/C and is also shown in Appendix 1 of reference [55]. The kinetics for each compound were evaluated, and 24 hours was found to be sufficient to attain equilibrium for each case.

A list of twelve alcohols with their adsorption capacities on filtrasorb-400 PAC and TSA's are summarized in Table 10. The straight-chain alcohols chosen were butanol, pentanol, hexanol and heptanol. Preliminary investigations show methanol, ethanol and propanol to be very poor adsorbers. This was expected since they are very soluble in

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water. Octanol and its isomers, however, were not water soluble to any great extent. For these reasons, these compounds were not included in this investigation.

Isomers of the linear alcohols were selected according to several criteria, not the least being availability. It was felt not only the length and extent of branching, but also the position of the hydroxyl group would effect the degree of adsorption.

The Langmuir adsorption capacity parameters Q^o, $\ln Q^o b$ are listed for each solute in Table 10. The correlation coefficient r is also given. In general, the data fit the Languir model well.

In an attempt to determine which solute characteristics correlate well with adsorption, the adsorption capacities were correlated with several parameters, often used in structure-activity correlations [60]: molecular weight (MW), total surface area (TSA), index of refraction (n_d), molar volume (V_m), molar refraction (MR), parachor ([P]), and the octanol-water partition coefficient (Log P). A summary of the values used for the parameters of each solute is presented in Table 11.

Linear Alcohols

The correlation coefficients of these parameters with the adsorption capacities for the four linear alcohols are presented in Table 12. Each of the parameters correlated well with the extent of adsorption as is expected. As the molecular weight increases, the linear molecules possess a proportionally larger non-polar surface, which results in higher adsorptivities. Such a strong correlation between Q^o, $\ln Q^o$ and $\ln Q^o b$ with MW, as well as with the other solute parameters, confirms the validity of our experimental data.

Branched and linear alcohols.

Likewise, these same correlations are carried out again for all twelve solutes, as shown in Table 13. In general, the parameters do not correlate nearly as well with adsorption capacity as do those for the linear group. In fact, the only parameters to correlate reasonably are TSA and the octanol-water partition coefficient, Log P.

TABLE 10. ADSORPTION ISOTHERM MEASUREMENTS FITTED TO THE LANGMUIRIAN MODEL FOR ALCOHOLS

Solute	MW	TSA $Å^2$	Concentration Range mmole/L	No. of Points	Q^o mmole/g	b $(mmole/L)^{-1}$	ln Q^o mmole/g	ln $Q^o b$	r
1. 1-butanol	74.1	251.5	.047 - .140	10	0.17(9)	20.1(8)	-1.72(0)	1.2(9)	0.96(0)
2. 2-methyl-1-butanol	88.2	267.2	.019 - .190	10	0.41(1)	30.7(2)	-0.88(9)	2.5(4)	0.98(7)
3. 1-pentanol	88.2	282.2	.023 - .133	10	0.43(7)	19.4(5)	-0.82(7)	2.1(4)	0.98(0)
4. 2,3-dimethyl-2-butanol	102.2	274.1	.032 - .151	13	0.59(8)	9.9(2)	-0.51(4)	1.7(8)	0.99(3)
5. 3,3-dimethyl-1-butanol	102.2	284.0	.020 - .108	11	0.53(4)	14.8(1)	-0.62(8)	2.0(7)	0.97(9)
6. 2-ethyl-1-butanol	102.2	290.0	.020 - .204	11	0.61(6)	45.2(5)	-0.48(5)	3.3(3)	0.96(1)
7. 2-methyl-3-pentanol	102.2	290.7	.014 - .139	14	0.46(5)	50.5(2)	-0.76(6)	3.1(6)	0.99(5)
8. 4-methyl-1-pentanol	102.2	300.4	.018 - .180	12	0.65(7)	51.2(4)	-0.42(1)	3.5(2)	0.99(4)
9. 1-hexanol	102.2	312.9	.009 - .161	10	0.78(0)	79.2(8)	-0.24(9)	4.1(2)	0.98(5)
10. 2,4-dimethyl-3-pentanol	116.2	301.2	.014 - .131	10	0.77(5)	40.6(4)	-0.25(5)	3.4(5)	0.99(0)
11. 3-ethyl-3-pentanol	116.2	302.0	.018 - .135	10	0.65(9)	41.2(2)	-0.41(7)	3.3(0)	0.98(3)
12. 1-heptanol	116.2	343.6	.005 - .127	10	1.03(9)	107.6(0)	0.03(8)	4.7(2)	0.99(5)

TABLE 11 SOLUTE PARAMETERS FOR THE ALCOHOLS

	Solute	MW	TSA $\AA^2$	V_m* cm^3/mole	MR† cm^{-3}	n_d‡	[P]§	Log P#
1.	1-butanol	74.1	251.5	91.52	22.152	1.399	205.3	0.87
2.	2-methyl-1-butanol	88.2	267.2	107.69	26.693	1.410	241.6	1.19
3.	1-pentanol	88.2	282.2	108.73	26.817	1.408	245.3	1.41
4.	2,3-dimethyl-2-butanol	102.2	274.1	124.09	31.245	1.418	274.2	1.29
5.	3,3-dimethyl-1-butanol	102.2	284.0	121.09	31.427	1.432	277.9	1.51
6.	2-ethyl-1-butanol	102.2	290.0	122.69	31.178	1.422	281.6	1.73
7.	2-methyl-3-pentanol	102.2	290.7	124.04	31.266	1.418	262.4	1.51
8.	4-methyl-1-pentanol	102.2	300.4	125.70	31.371	1.413	281.6	1.73
9.	1-hexanol	102.2	312.9	125.26	31.440	1.416	285.3	1.95
10.	2,4,dimethyl-3-pentanol	116.2	301.2	140.20	35.849	1.425	314.2	1.83
11.	3-ethyl-3-pentanol	116.2	302.0	138.22	35.662	1.429	317.9	2.05
12.	1-heptanol	116.2	343.6	141.31	35.909	1.424	325.3	2.49

* V_m = MW/density; densities from Ref. [61]

† $MR = [(n_d^2-1)/n_d^2+2)] \times V_m$

‡ Data from Ref. [58]

§ Data from Ref. [62]

\# Data from Ref. [63]

TABLE 12. CORRELATION COEFFICIENT r FOR LANGMUIRIAN ADSORPTION PARAMETERS VS. SOLUTE PARAMETERS FOR THE LINEAR ALCOHOLS ONLY*

Adsorption Coefficient	Molecular Weight	TSA $\AA^2$	η_d	V_m cm^3/mole	MR cm^{-3}	[P]	Log P
Q^o	0.99(8)	0.99(8)	0.99(8)	0.99(8)	0.99(8)	0.99(8)	0.99(8)
ln Q^o	0.97(4)	0.97(4)	0.97(4)	0.97(4)	0.97(5)	0.97(4)	0.97(4)
ln $Q^o b$	0.97(9)	0.97(9)	0.97(8)	0.97(8)	0.97(9)	0.97(9)	0.97(9)

* Compounds 1,3,9 and 12 from Table 10.

TABLE 13. CORRELATION COEFFICIENT r FOR LANGMUIRIAN ADSORPTION PARAMETERS VS. SOLUTE PARAMETERS FOR ALL TWELVE ALCOHOLS.*

Adsorption Coefficient	Molecular Weight	TSA $\AA^2$	η_d	V_m $cm^3/mole$	MR cm^{-3}	[P]	Log P
Q^o	0.86(1)	0.93(9)	0.62(7)	0.88(9)	0.86(9)	0.91(5)	0.93(3)
$\ln Q^o$	0.89(7)	0.87(5)	0.71(1)	0.91(6)	0.90(3)	0.92(5)	0.88(6)
$\ln Q^o b$	0.71(3)	0.92(6)	0.44(1)	0.74(8)	0.71(7)	0.76(3)	0.91(1)

* Compounds 1 - 12 from Table 10.

The partition coefficient of a solute distributed between a relatively non-polar phase such as octanol and a polar phase such as water should correlate with the adsorptivities of the alcohols onto the non-polar activated carbon sorbent from the polar aqueous solution.

The adsorption parameter Q^o is plotted against molecular weight in Fig. 13 with a correlation coefficient of r=0.86(1). Q^o is a measure of the total amount of solute the carbon can adsorb at saturation. Although molecular weight (and the other solute parameters) correlated well with Q^o for the linear alcohols, it is not a useful parameter when branched compounds are considered. From Fig. 13, as 1-hexanol (MW=102.2) becomes less linear and more branched, Q^o decreases. The available solute surface area for adsorption decreases as the molecule becomes less linear and more spherical. In each case, the straight-chained solute was more highly adsorbed than the branched form with the same molecular weight. In fact, as the length of the chain increases, the extent of adsorption becomes increasingly less sensitive to characterization by molecular weight alone.

Q^o is correlated with TSA in Table 13. With a correlation coefficient of r=0.93(9), TSA is a much more reasonable parameter to characterize adsorption than molecular weight. While the correlation coefficients for Q^o with TSA and MW are not significantly different at 95% confidence, they are statistically different at 80% confidence (for twelve sample pairs). In general, as the surface area of the solute decreases, the adsorption decreases. This parameter takes into account the effect of branching and the location of the various side-chains.

The same trend is observed when ln $Q^o b$ for the twelve alcohols is plotted against both molecular weight and TSA. From Fig. 14 ln $Q^o b$ and molecular weight has a correlation coefficient r=0.71(3). However, from Fig. 15 , plotting ln $Q^o b$ against TSA gives a much better correlation, with r=0.92(6). This difference is significant at 95% confidence.

In Fig. 16 , these relationships become clear. The effect of branching on the adsorption of alcohols with the same molecular weight is shown. The adsportion data for each compound with molecular weight 102.2 is fit to the linearized form of the Langmuir model. The slope of each line ($1/Q^o b$) is a

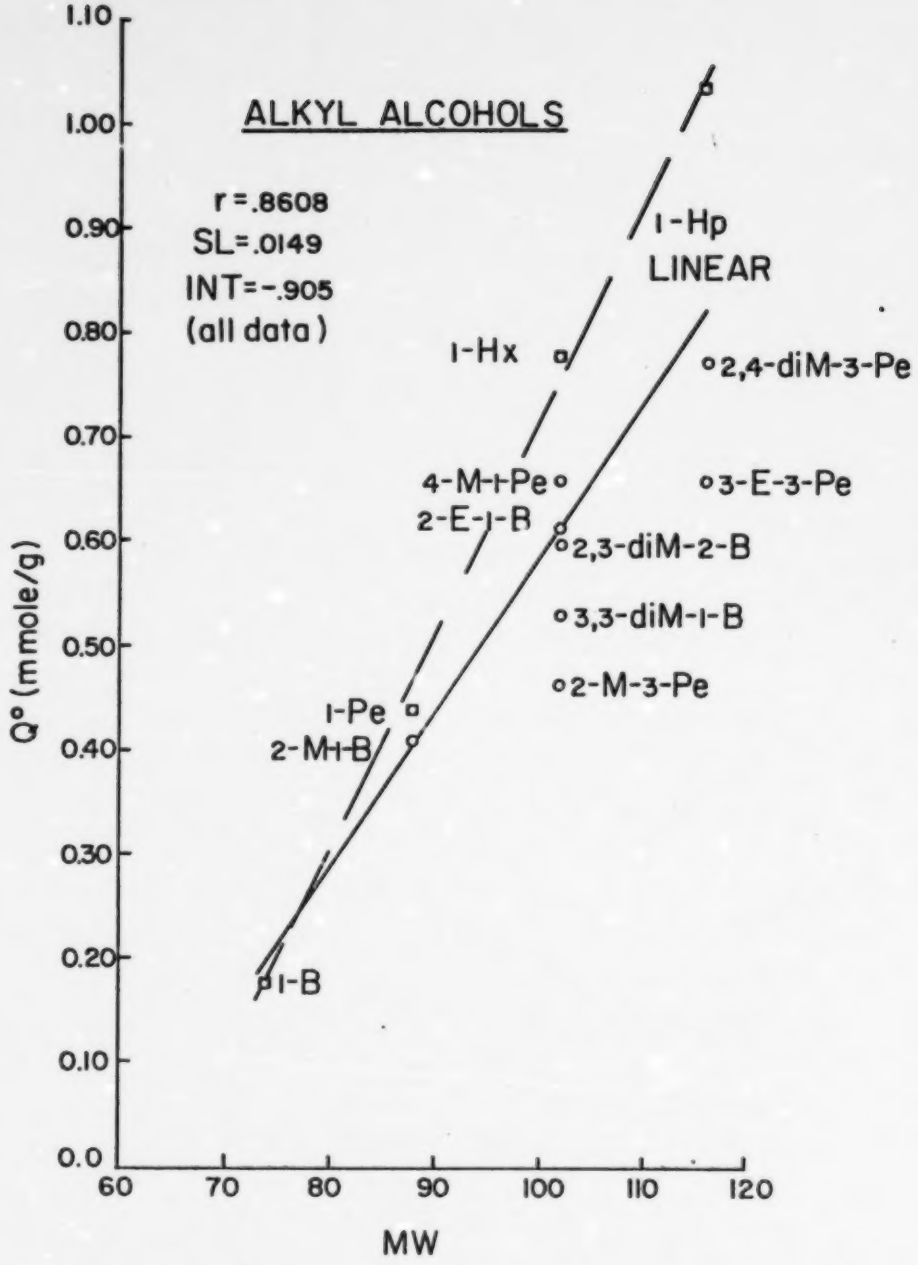

Fig. 13. Langmuir saturation constant (Q^o) versus MW for linear and non-linear alcohols. Abbreviated symbols are used to describe compounds listed in Table 10.

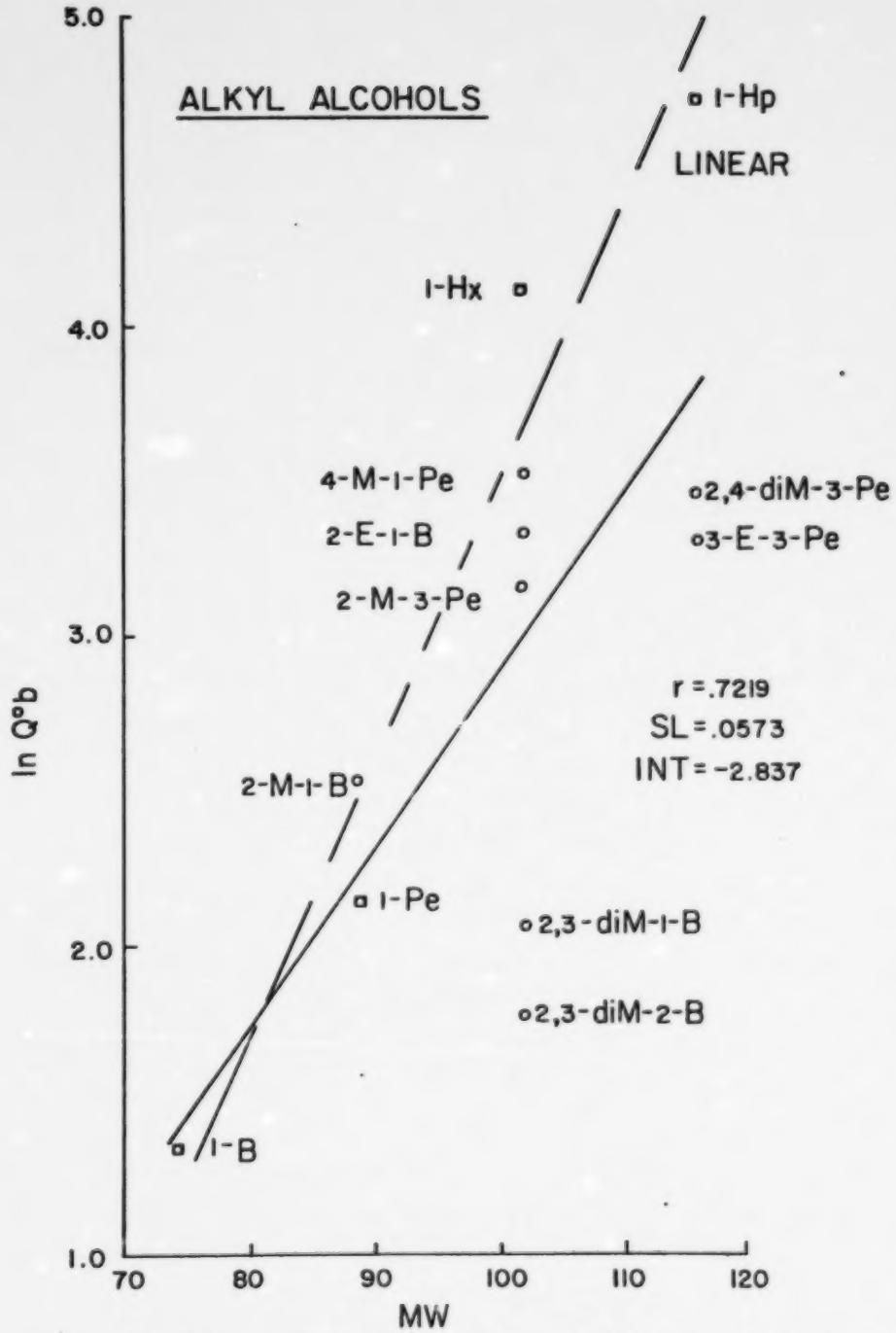

Fig. 14. Adsorption capacity, ($\ell nQ^{o}b$) versus MW for linear and non-linear alcohols.

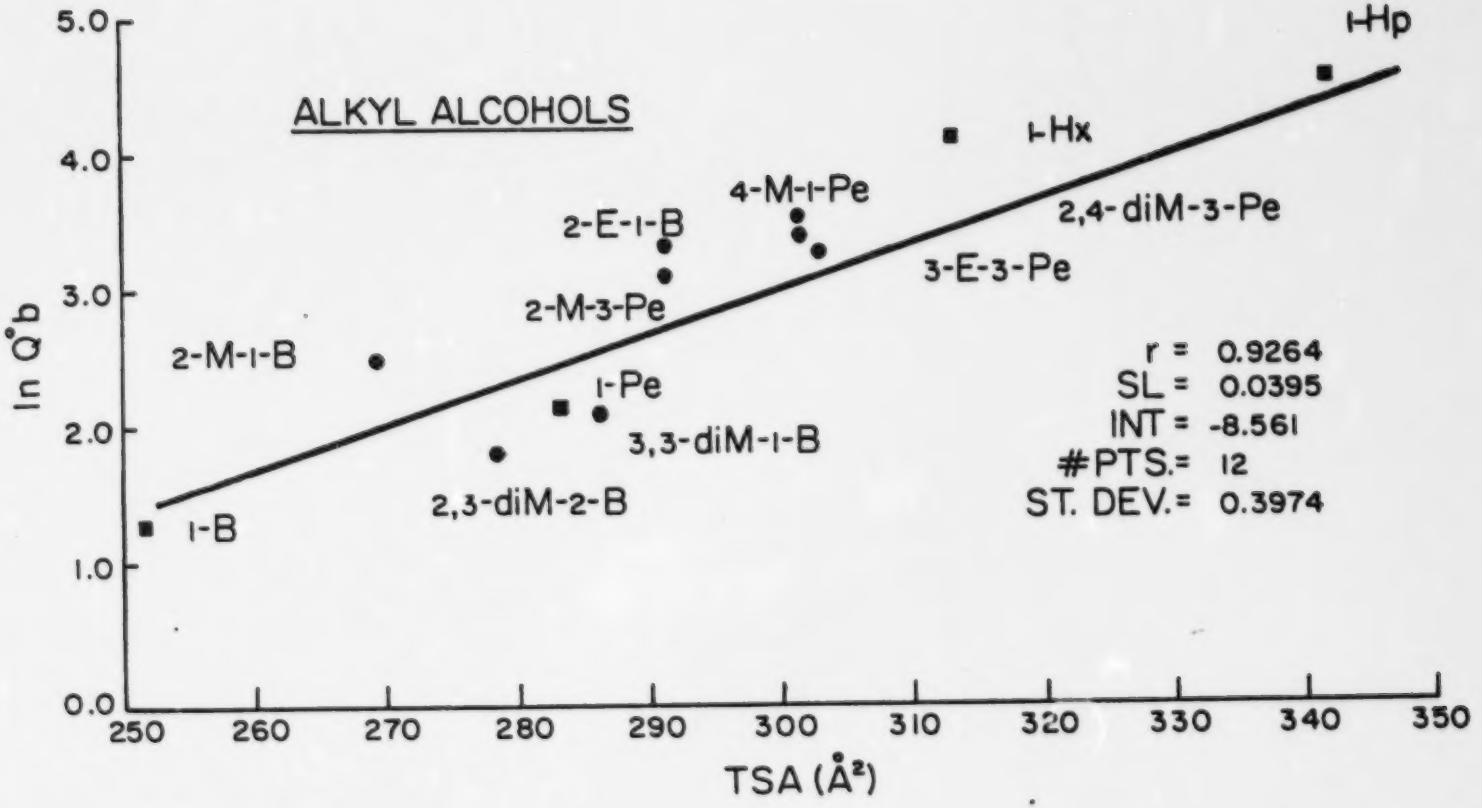

Fig. 15. Adsorption capacity (ℓnQ^c), versus cavity surface area for linear and non-linear alcohols.

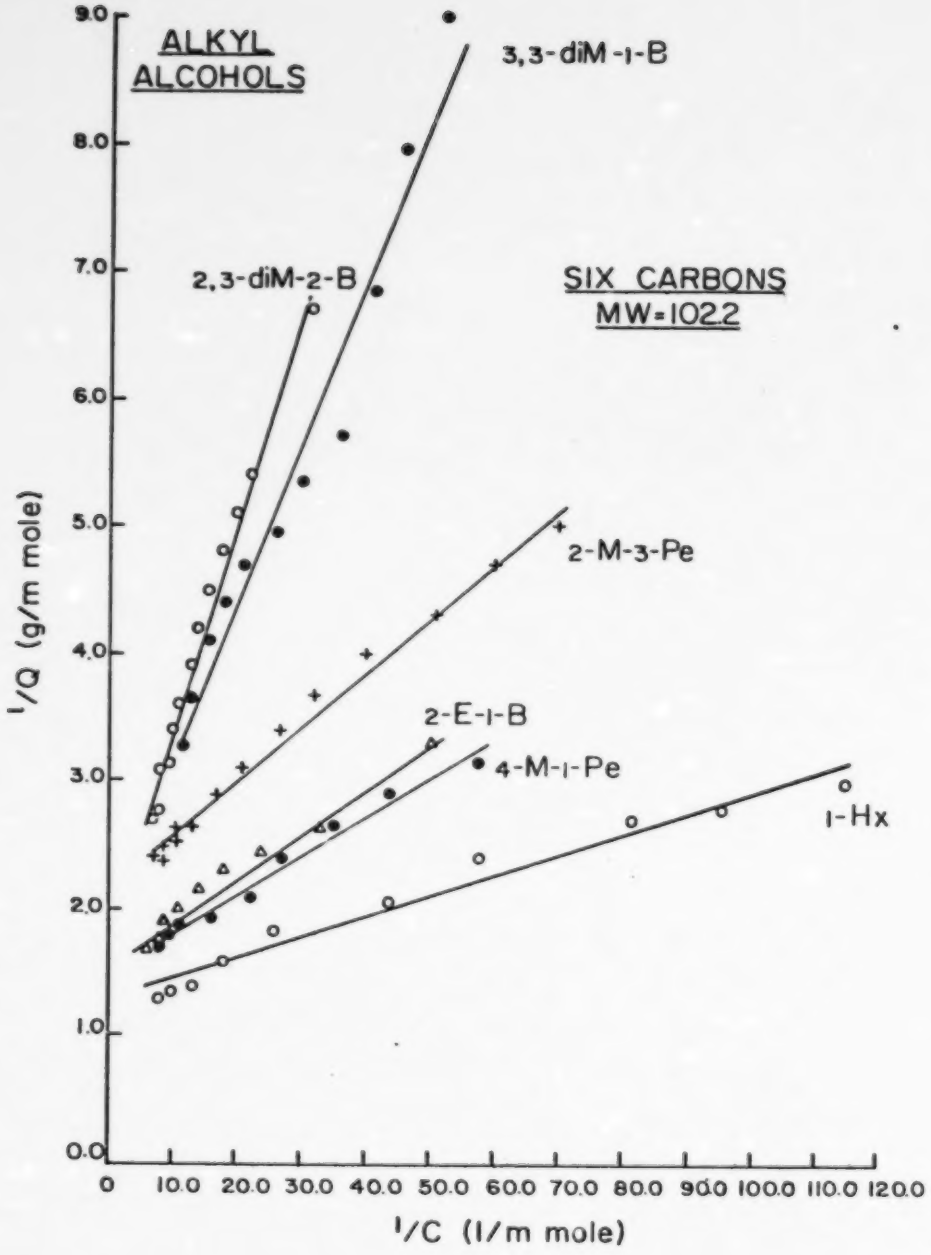

Fig. 16. Langmuir adsorption data for alkyl alcohols with MW = 102.2.

measure of the compound's ability to adsorb to the carbon in dilute solution. The lower the slope, the stronger the adsorption. The region of low solute concentration (high 1/C values) is usually of concern in the environment and is the region to which the solvophobic theory best applies.

The effect of branching is clearly evident from the data presented in Fig. 16, where the linear isomer is adsorbed more strongly than any of its branched isomers. Since the linear isomer has the highest cavity surface area with the hydroxyl group attached to the first carbon atom, the non-polar surface area available for contact and adsorption with the sorbent is probably the largest. Also, solvation about a hydroxyl-group attached to the first carbon atom is probably easier than about a hydroxyl-group attached to some intermediate carbon atom.

Reducing the number of carbons in the backbone reduces the adsorption capacity and cavity surface area of the isomers (from 1-hexanol to 4 methyl-1-pentanol to 2-ethyl-1-butanol). For an isomer with a given number of carbon atoms in the backbone, moving the hydroxyl-group from the first to an intermediate carbon also reduces the cavity surface area and the adsorption capacity (from 4-methyl-1-pentanol to 2-methyl-3-pentanol; and 3,3-dimethyl-1-butanol to 2,3-dimethyl-2-butanol). Attaching the hydroxyl-group to an intermediate carbon atom may also have the effect during (adsorption and) solvation of lifting the solute molecule away from the carbon surface at this intermediate carbon resulting in reduced adsorption. Clearly, a balance between the solvation forces at the hydroxyl-sight of the solute with the non-polar interactive forces between the hydrophobic regions of the solute and the sorbent, surface is important in understanding subtle structural effects on the adsorption process. This is precisely the *raison d'être* of the cϕ-theory. The same trends are observed for the compounds with molecular weight 116.2 as seen in Fig. 17. The linear alcohol 1-heptanol is much more strongly adsorbed than either 3-ethyl-3-pentanol or 2,4-dimethyl-3-pentanol.

It is interesting to note that 2-ethyl-1-butanol is slightly better adsorbed ($\ln Q^{o}b$) than 3-ethyl-3-pentanol. This observation illustrates again the importance of the location of the hydroxyl and branching group. 3-ethyl-3-pentanol would be expected to have considerably stronger adsorption

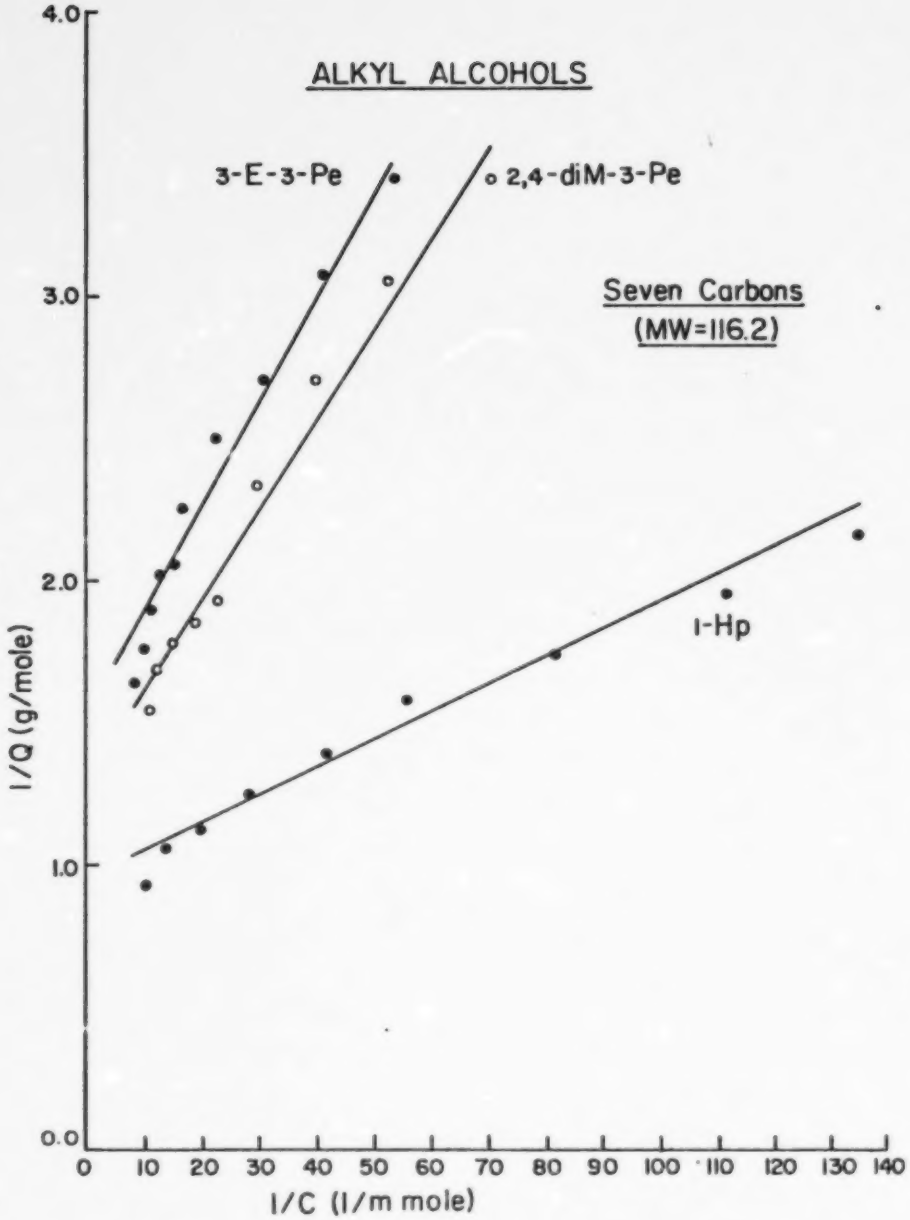

Fig. 17. Langmuir adsorption data for alkyl alcohols with MW = 116.2.

than 2-ethyl-1-butanol based on molecular weight alone, if the position of the hydroxyl group was of negligible influence. Shifting the hydroxyl group from the first to the third position, however, results in reduced adsorption capacity by effectively reducing the solute area available for adsorption.

In summary, the adsorption capacity decreases (slope increases) for each isomer of a homologous series with increased branching or decreased cavity surface area.

MULTICOMPONENT ADSORPTION

The simultaneous adsorption of two or more components from an aqueous solute mixture is most often observed in practical systems. Clearly, the usefulness of the cϕ-theory will depend eventually on its ability to rank-order the adsorption of solutes from multicomponent systems. To sucessfully use the cϕ-theory, it must be adapted and evaluated for multicomponent adsorption. Using single solute adsorption isotherms, the Ideal Adsorbed Solution (IAS) theory has been effectively used for predicting adsorption isotherms from bisolute mixtures. Three models for describing the single solute isotherms are incorporated and compared in the IAS-Theory for the adsorption of a bisolute system (propyl phenol and phenol).

Another approach involves a multi-step fitting routine whereby the mulicomponent adsorption isotherms are described by an empirical Eqn (21) with a known set of parameters. The usefulness of this approach is to obtain interpolative rather than predictive results. This approach is evaluated using the same bisolute system described above.

Experimental adsorption results for a penta-solute system (phenol, 2-methyl phenol, ethyl phenol, 4n-propyl phenol, and 2-butyl phenol) is also presented. Detailed modelling however is not attempted. A semi-empirical surface tension approach is used to formulate a multi-step design procedure for predicting the multicomponent adsorption of each solute in the mixture.

Bisolute Adsorption

Ideal adsorbed solution theory

The two solute aqueous system phenol/4-propyl phenol was used to test the above three methods. Of the two, 4-propyl is more strongly adsorbed, as shown by the isotherm constants:

	Freundlich		Langmuir	
	n	K_f	Q^o	b
Phenol	2.65(4)	2.2876	0.85(9)	87.2
4-Propyl Phenol	9.06(7)	2.0723	1.58(0)	354.2

The effect of phenol on the adsorption of propyl phenol was predicted fairly well by the IAS theory as shown in Figs. 18, 19, and 20. However, the effect of propyl phenol on the adsorption of phenol was not predicted well in any of the three variations compared. For example, see Table 14 for the Freundlich case only.

A contributing reason to this failure can be seen from Eqn (29). Since propyl phenol is preferentially adsorbed, its mole fraction in the surface phase will be close to unity, leaving the mole fraction of phenol very small. Now the loading of phenol must be calculated at $C_i^o = C_i/Z_i$. Therefore, C_i^o will be very large for phenol, well beyond the limits of its isotherm. No matter what functional form is used, the extrapolation of an isotherm over a long distance can introduce significant error.

The problem of extrapolation is also important when trying to characterize the numerical form of the isotherm, or spreading pressure. For a given bounded set of data, any one of a number of equations can be fit (e.g., linear, nth degree polynomial, cubic spline, etc.). However, erroneous data points can result in totally misleading values when extrapolating. A clear example of this is shown in Fig. 21, which plots q_i/C_i, the integrand of the spreading pressure equation vs. C_i. The dotted line is the analytical result from the Freundlich equation, the solid line is the same for the Langmuir equation, and the data points are the experimental values. The last data point appears to be in error with respect to the analytical line. However, a perfectly good quadratic or higher order polynomial could be fit to it, resulting in the curve going to $+\infty$, or $-\infty$, instead of zero.

The strange behavior of the piece-wise Freundlich equation, Fig. 20, can be readily explained. This method fits Freundlich constants to every segment of the isotherm, which is then used to calculate the spreading pressure (i.e., the area under the curve in Fig. 21). Therefore, the

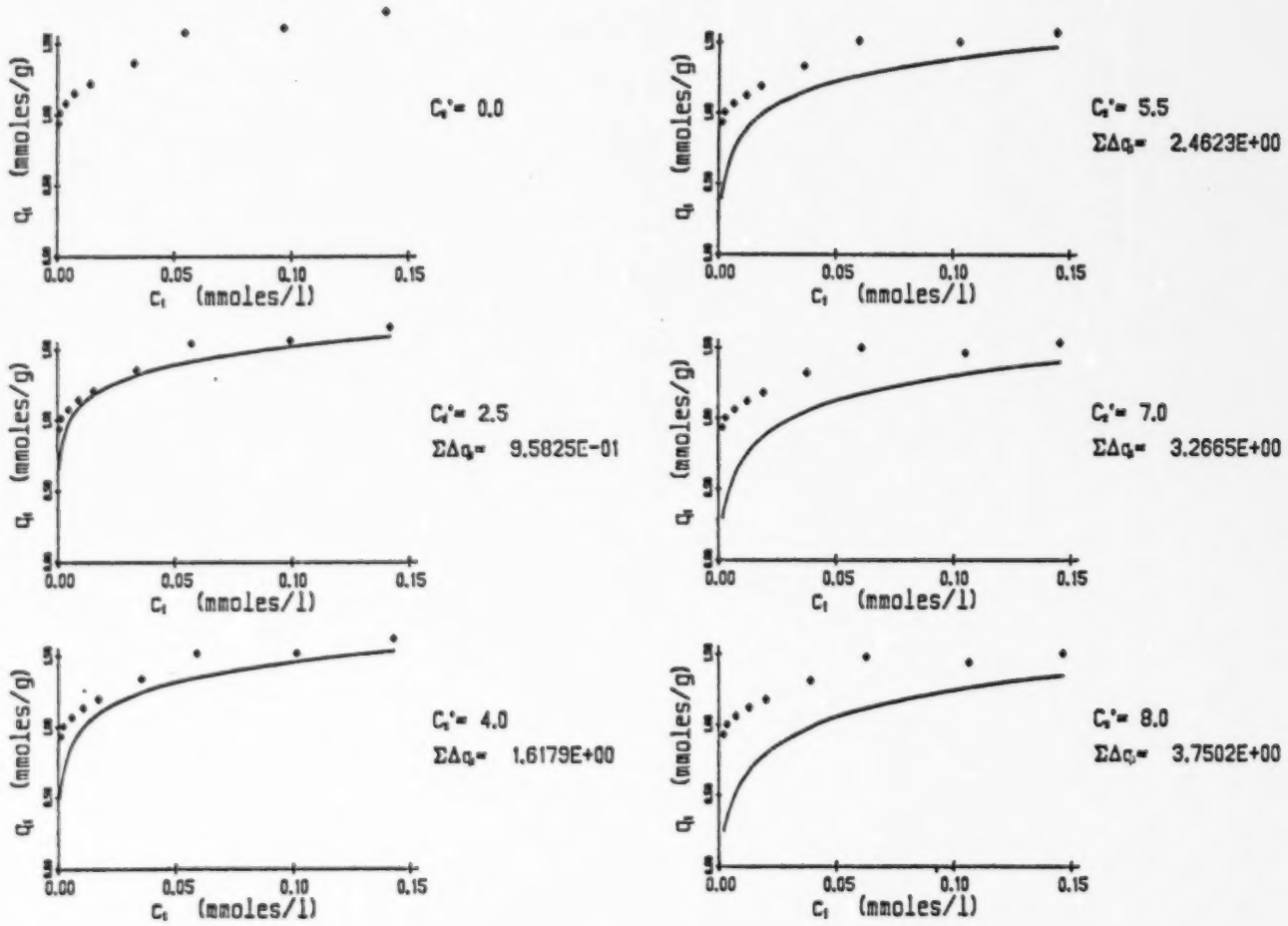

Fig. 18. Bisolute isotherms for adsorption of 4n-propyl phenol (1) in the presence of phenol (2), as calculated from the IAS theory, and Freundlich equation. Solid line represents theory, and the dots are measured experimental values.

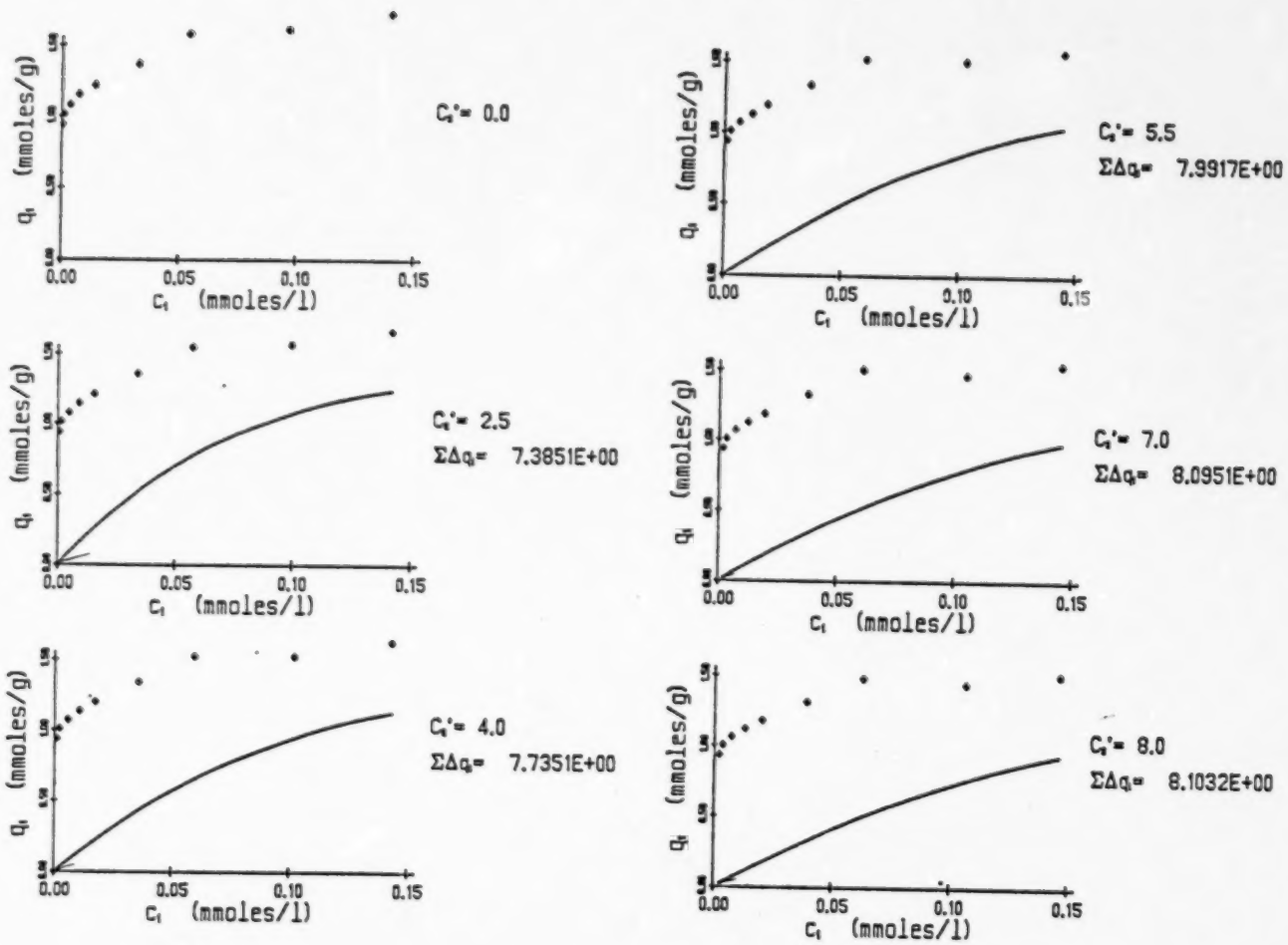

Fig. 19. Bisolute isotherms for adsorption of 4n-propyl phenol (1) in the presence of phenol (2), as calculated from the IAS theory, and Langmuir equation.

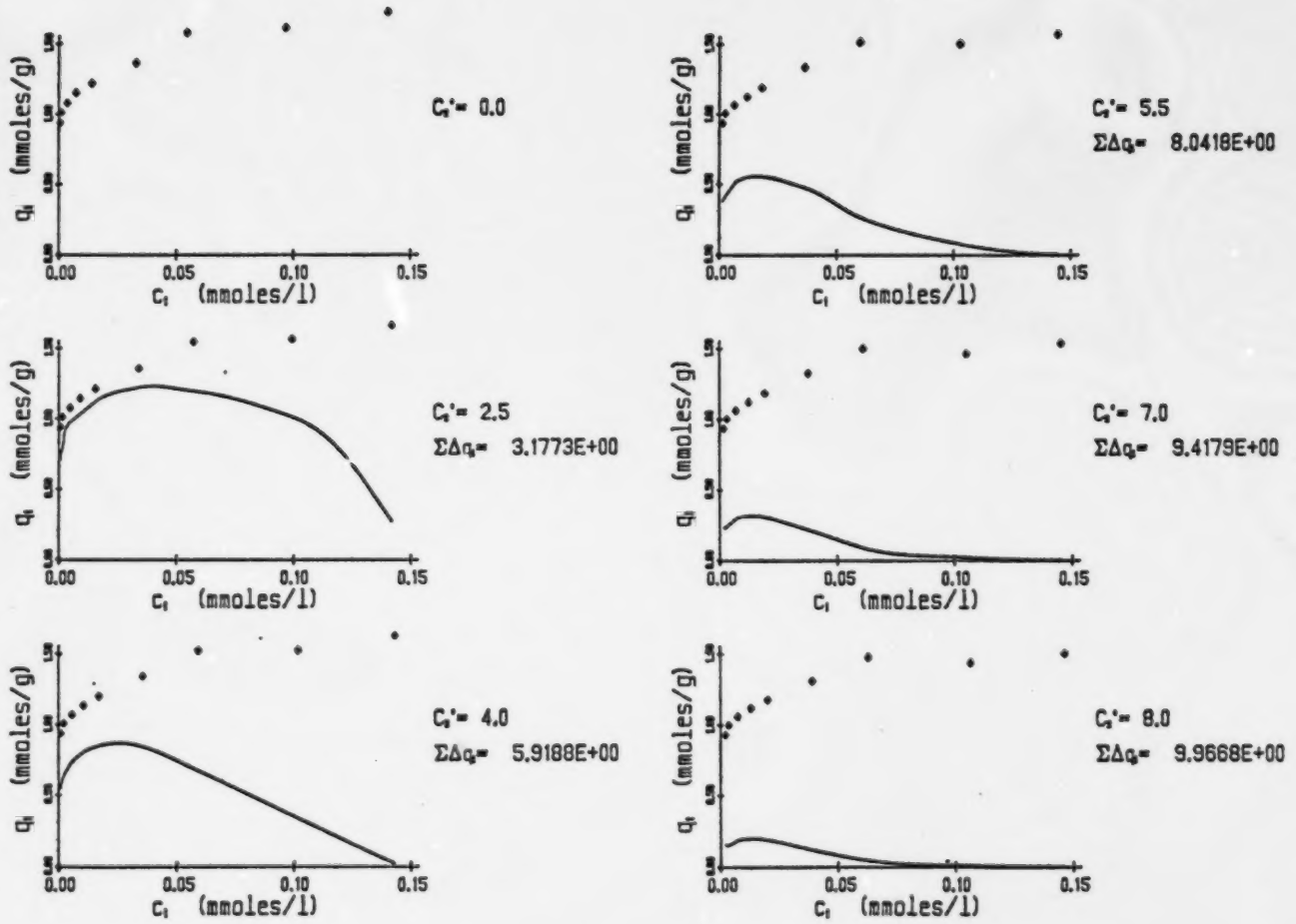

Fig. 20. Bisolute isotherms for adsorption of 4n-propyl phenol (1) in the presence of phenol (2), as calculated from the IAS theory, and piece-wise Freundlich equation.

TABLE 14. EFFECT OF 4n-PROPYL PHENOL(2) ON THE ADSORPTION OF PHENOL(1) AS CALCULATED BY THE SINGLE FREUNDLICH MODEL *

C_1 mmole ℓ^{-1}	C_2 mmole ℓ^{-1}	q_1, theory mmoles/g	q_1, experiment† mmoles/g
0.100	0.153	0.01(5)	1.14(3)
0.086	0.108	0.13(4)	0.81(0)
0.070	0.069	0.01(2)	0.73(3)
0.056	0.036	0.01(1)	0.66(8)
0.046	0.014	0.01(0)	0.60(1)
0.031	0.005	0.00(9)	0.59(0)
0.026	0.001	0.00(9)	0.53(1)
0.020	0.000(4)	0.00(9)	0.49(1)
0.013	0.000(1)	0.00(7)	0.46(2)
0.012	0.000(6)	0.00(7)	0.42(1)

* $C_2^{'}$ is the initial concentration of phenol; $C_2^{'}$ = 0.20 mmoles/ℓ

† $\Sigma|q_1$, experiment - q_1, theory | = 6.3474 mmoles/g

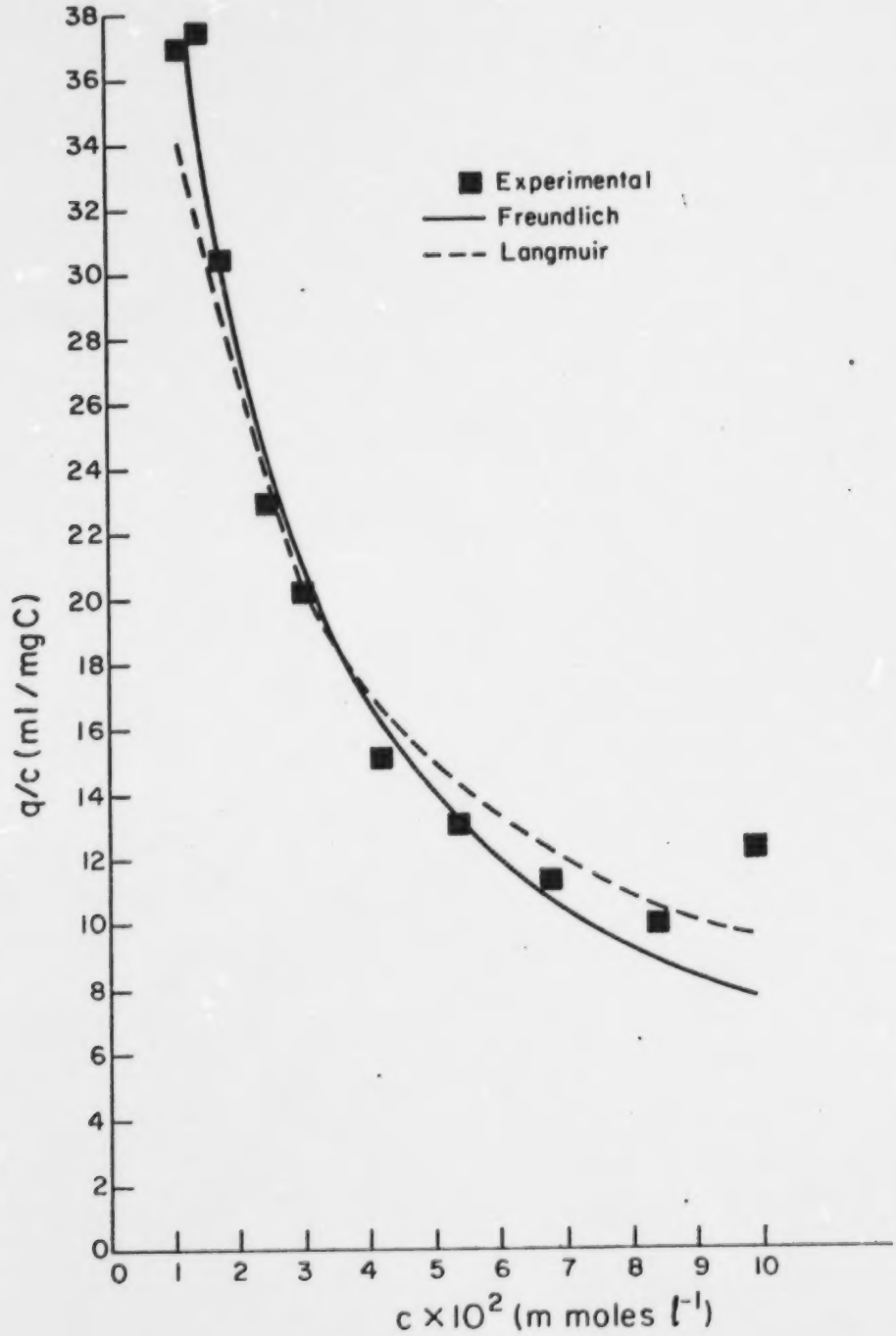

Fig. 21. Integrand of the spreading pressure equation, for experiment, and calculated from Freundlich and Langmuir constants.

analogous curve for this method would pass through every point of Fig.21 But since the last point is higher than the one before, the value of q_i/C_i would go to infinity (rather than zero as in the other two cases) as C_i increases.

If this last point is omitted from the phenol isotherm in Fig. 22 then the piece-wise results for propyl phenol adsorption improve dramatically as shown in Fig. 23.

While the piece-wise Freundlich method would help to characterize adsorption isotherms over a wide range of concentrations, it was found to yield only marginal improvements for the situations studied in this section. See Table 15. The advantage of the single Freundlich equation is its simplicity. In general, a higher order polynomial would provide a better fit to experimental data in the least-squares sense, eventually the good fit would be due to characterizing experimental error of the system.

In this section, only the effect of phenol on 4-propyl phenol could be predicted with any accuracy. A less severe test of this theory would be to choose two components of closer adsorbability, and calculate the effects of each component on the other. In addition the effects of non-idealities could be investigated further. In particular, independent values for the liquid phase activity coefficient could be used, and various functional forms of the adsorbed phase activity coefficients could be examined.

Empirical model

The equations and method of calculation for fitting the empirical model, Eqn. (41) to a bisolute adsorption experiment are presented in the theoretical section. The procedure is fitted to a 4-propyl phenol (1)/phenol (2) mixture adsorption experiment in which the isotherm of solute (1) is measured as a function of different constant concentrations of solute (2) and vice versa. The results of the fit are expressed through the empirical parameters a_{ij} and b_{ij} and compared in Table 16 with a similar experiment by Fritz and Schlünder [38] using a 4-nitro phenol (1)/phenol (2) mixture. The value of the constants for the two systems are similar.

Pentasolute Adsorption

In correlating adsorption capacity ($\log \bar{p}_i$) for a homologous series versus cavity surface area (TSA) for the simplified cϕ-model, it was

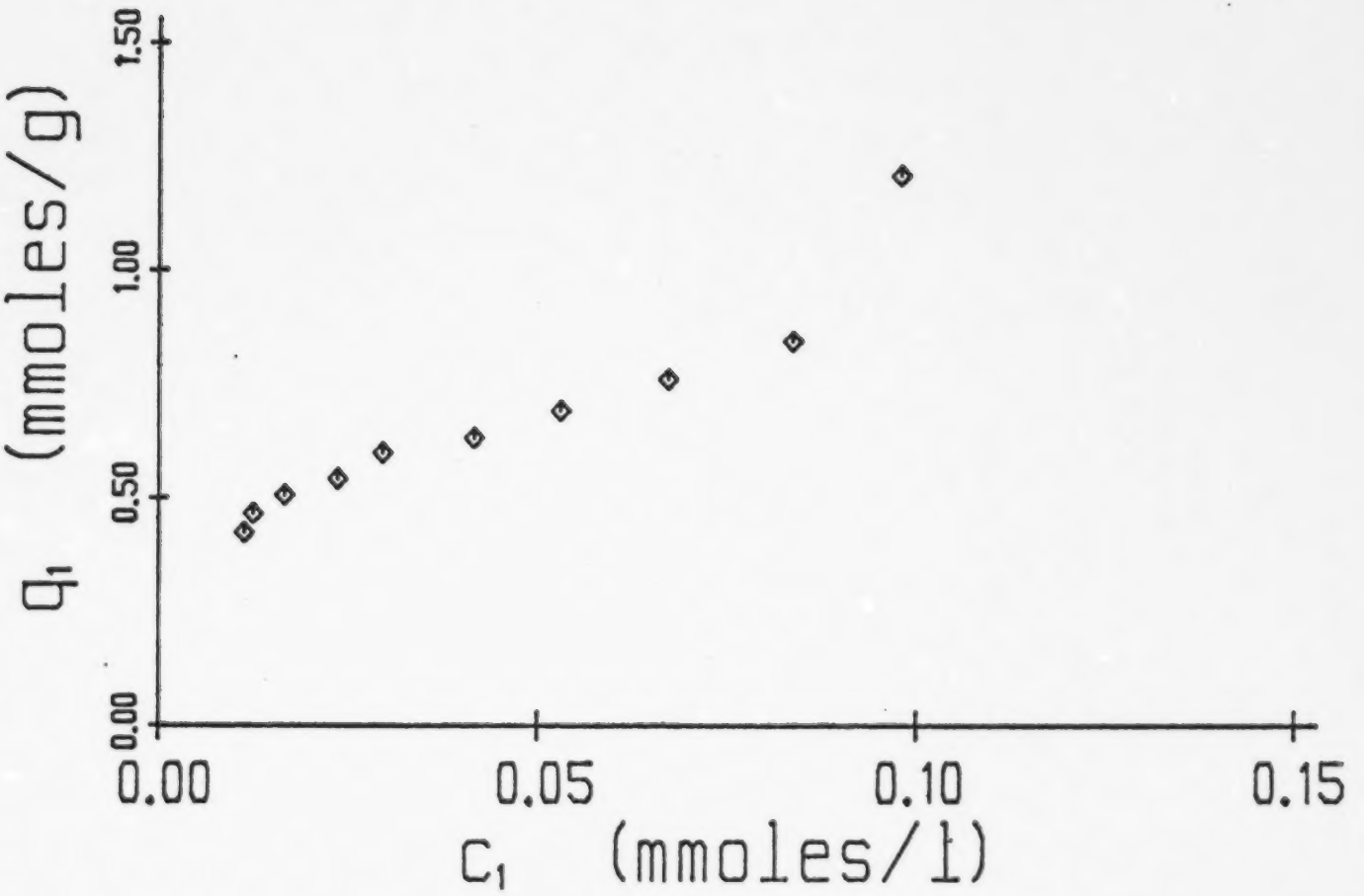

Fig. 22. Phenol isotherm at 20±1°C on PAC.

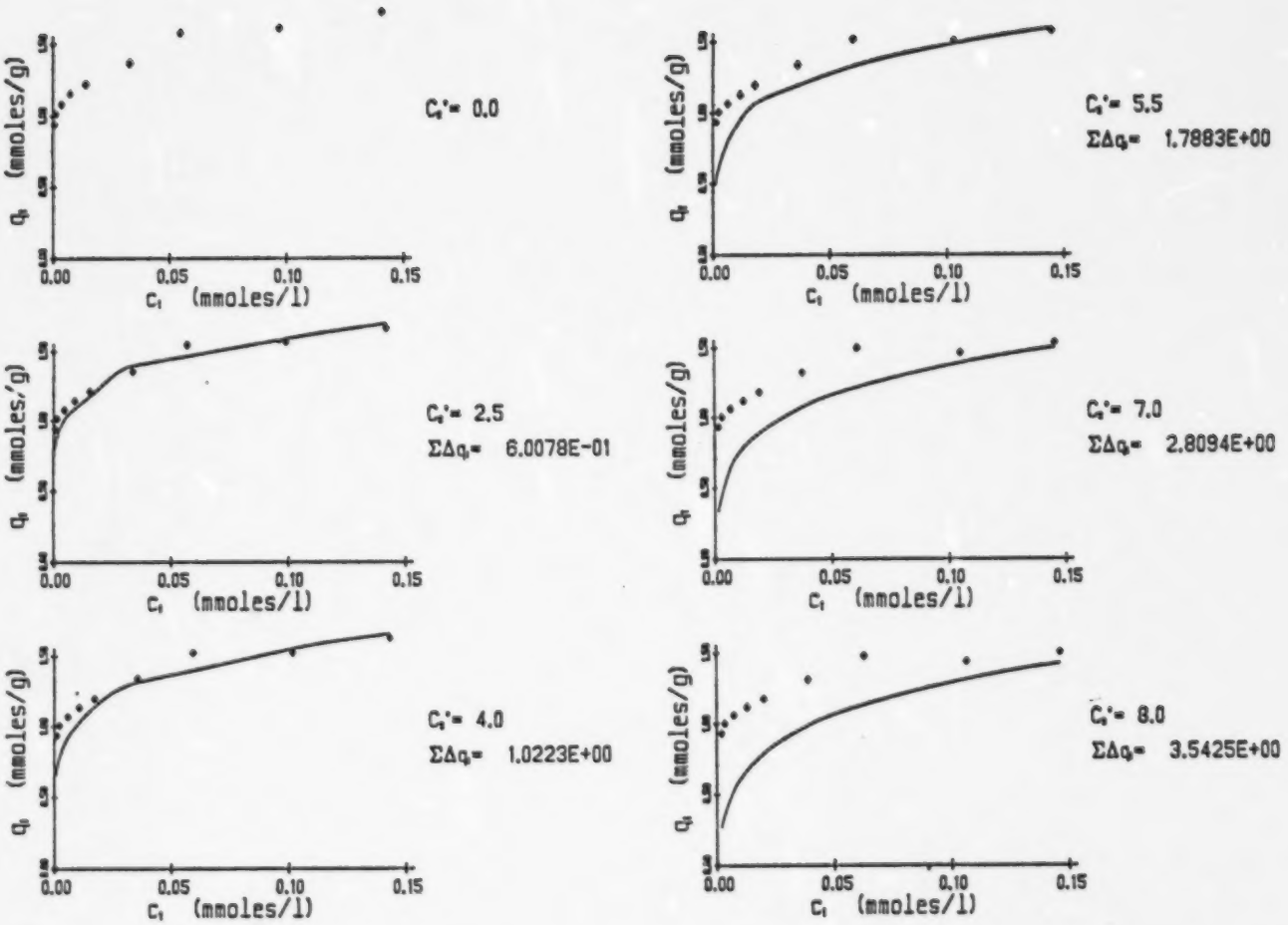

Fig. 23. Bisolute isotherms for adsorption of 4-propyl phenol (1) in the presence of phenol (2), as calculated from the IAS theory, and piece-wise Freundlich equation, omitting stray point from phenol isotherm.

TABLE 15. PREDICTIVE ERROR OF EFFECT OF PHENOL(2)
ON THE ADSORPTION OF 4-PROPYL PHENOL(1)

C_2' * mmole ℓ^{-1}	$\Sigma\lvert q_1$, experiment $-q_1$, theory$\rvert$ mmole/g			
	Single Freundlich	Single Langmuir	Piece-wise Freundlich	
2.5	0.958	7.385	3.177	0.601†
4.0	1.618	7.735	5.919	1.022
5.5	2.462	7.992	8.042	1.788
7.0	3.327	8.095	9.418	2.809
8.0	3.750	8.103	9.967	3.543

* C_2' is the initial concentration of phenol.

† Omit last point from phenol isotherm; see Fig.22.

TABLE 16. EMPIRICAL CONSTANTS FOR REPRESENTING BISOLUTE ADSORPTION ACCORDING TO EQUATION (41)

SOLUTES	ACTIVATED CARBON	CONSTANTS									
		a_1	b_1	b_{11}	a_{12}	b_{12}	a_2	b_2	b_{22}	a_{21}	b_{21}
4-propyl phenol (1) and phenol (2)	F-400 (powdered)	2.07	0.11	0.89	0.061	2.29	1.77	0.31	0.69	2.49	0.88
4-nitro phenol* (1) and phenol (2)	F-300 (granular)	2.05	0.13	0.50	0.022	1.10	1.45	0.21	0.70	9.30	0.79

* Results taken from [38].

discovered by Belfort [16,35] that the slope of the linear correlation decreased when comparing pure with mixed solutions. New data illustrating this effect is shown in Fig. 24. Eqn (18) suggests that this slope is proportional to the interfacial tension between water and the hydrophobic surface, γ_{wh} or more generally the slope is given by $m = -\frac{N\gamma_{wh}}{RT}[(1-q)-g]$, where q is the curvature correction and g is the fractional surface area change resulting in the association adsorption process.

A possible method of confirming the γ_{wh}-dependence on adsorption capacity is to study the adsorption of a single pure compound in different aqueous solutions with different interfacial tensions. This is shown for 2-butyl phenol in Fig. 25, where the adsorption capacity decreases linearly with increasing methanol concentration or decreasing interfacial tension. Since methanol adsorption is so low it could not be measured, competition is not thought to be significant.

Using the data in Fig. 24 and the measured surface tension at saturation for each member of the homologous series, Fig.26 was constructed for use with the predictive design procedure described in the theoretical section. The linear correlation between adsorption ratio and reduced surface tension differences is relatively good (r=0.9838).

While this treatment is phenomenological in nature, the abscissa of Fig. 26, which is the fractional reduction of surface tension due to the i^{th} solute, is directly related to the spreading pressure, π, of that solution. Thus, this treatment parallels other more classical thermodynamic approaches such as the Ideal Adsorbed Solution Theory [43] which relate single solute spreading pressure to that of a mixture.

This approach could be very useful in quantitatively ranking the multicomponent adsorption capacity of a homologous series, such as alkyl phenols found in coal treatment effluent.

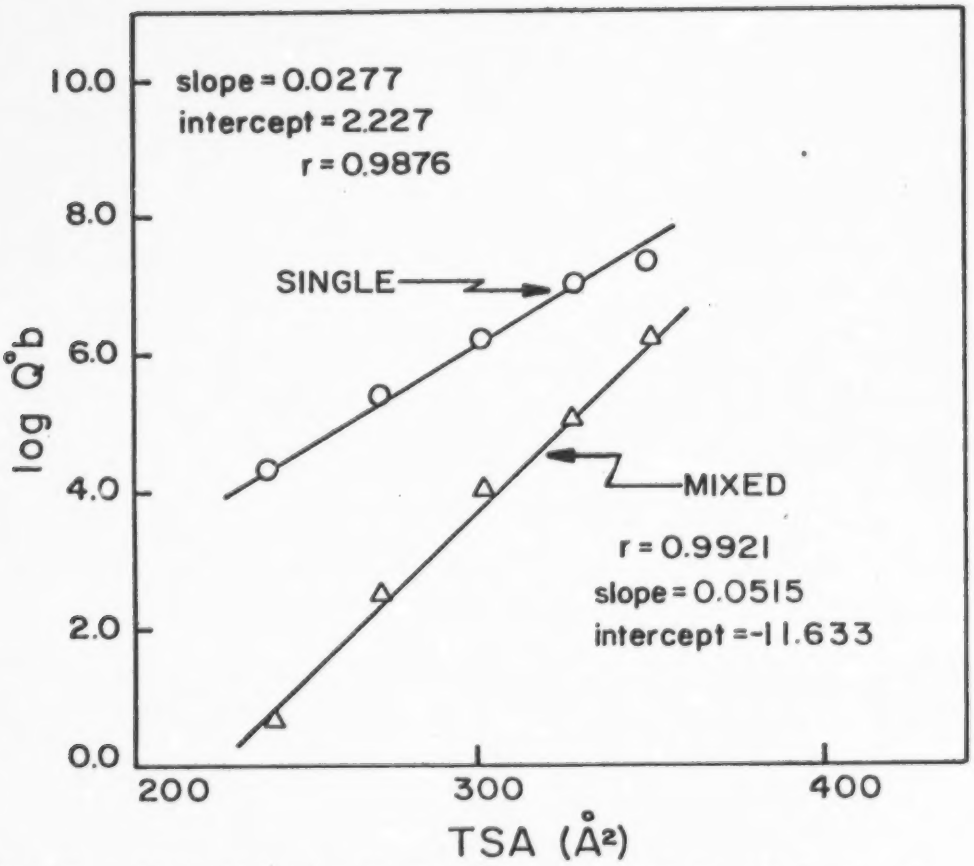

Fig. 24. Adsorption capacity ($\ell n Q^{o}b$) versus TSA for alkyl phenols singly, and in penta-solute mixture.

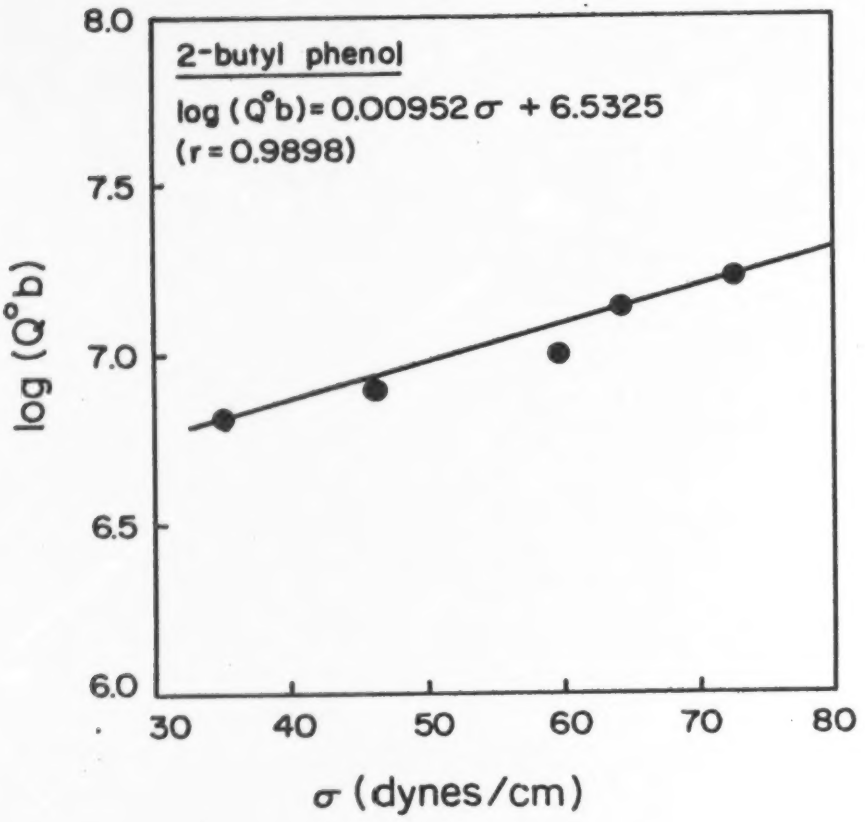

Fig. 25. Adsorption capacity (log $Q^{o}b$) versus surface tension for 2-butyl phenol.

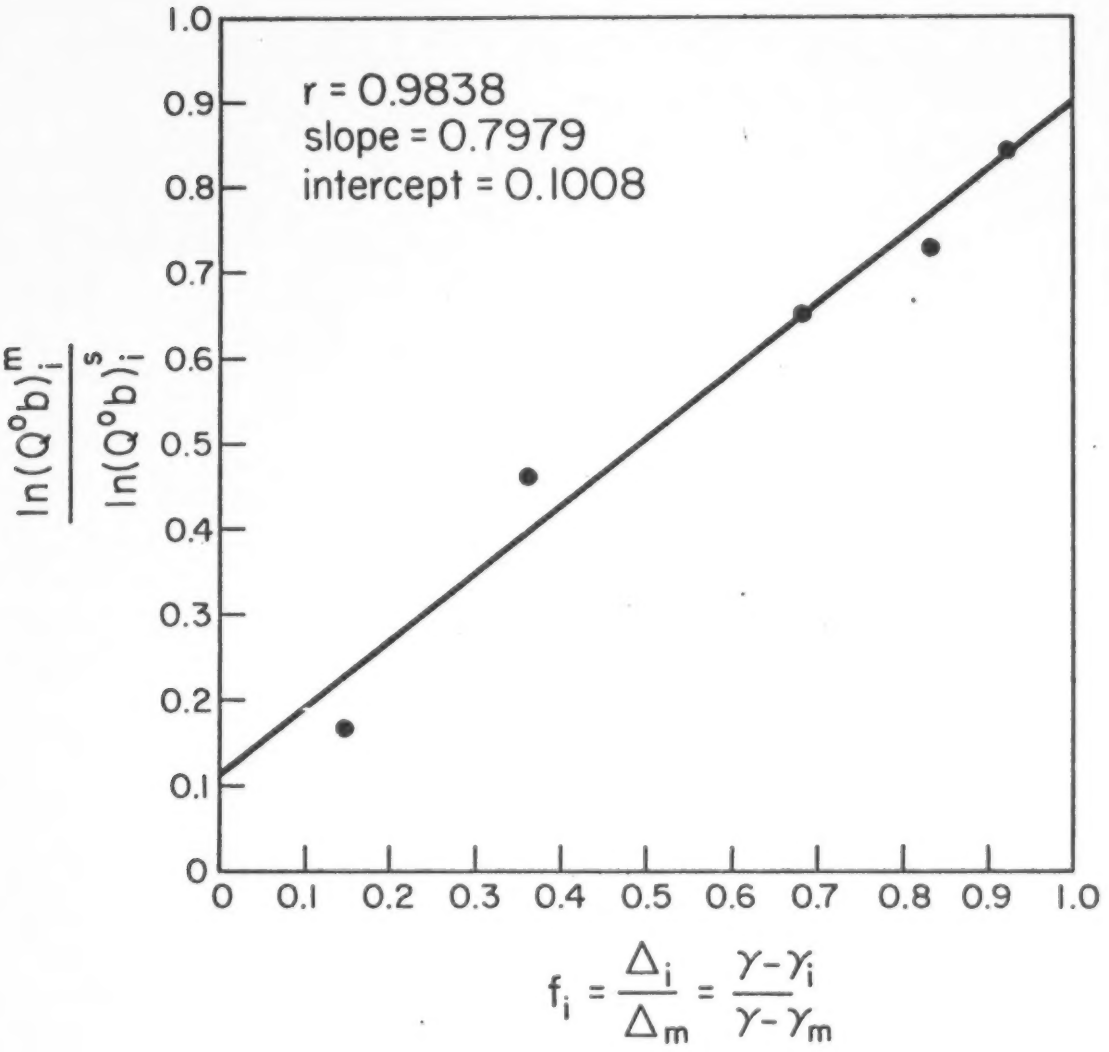

Fig. 26. Ratio of alkyl phenol adsorption capacities in a mixture to that in single solute system, versus fractional reduction of surface tension.

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APPENDIX A

INTERACTION PROCESS FOR THE SOLVOPHOBIC THEORY

The interaction terms comprising of the overall standard unitary free energy change as expressed in Eq. (7) in the text can be calculated with a knowledge of the physicochemical properties of each species using detailed expressions from the literature. In Table A-1, the cavity $\Delta G^{net}_{cav,i}$ and the interaction terms ($\Delta G^{net}_{vdw,i}$ and $\Delta G^{net}_{es,i}$) are defined for species i. The table was compiled from Halicioğlu [31].

TABLE A-1. EXPRESSION DEFINING THE UNITARY FREE ENERGY CHANGE FOR THE INTERACTION PROCESSES

Interaction Process	Free Energy Designation	Expression	Equation Number
Cavity Formation *	$\Delta G^{net}_{cav,i}$	$K^e_i A_i \gamma_{w,i}(1-W)N$	A-1
Solvent-Solute Interaction van der Waals†	$\Delta G^{net}_{vdw,i}$	$-f(\xi,\ell)\Delta_i D_i DB_i$	A-2
Electrostatic ‡	$\Delta G^{net}_{es,i}$	$-\frac{N}{2}\frac{\mu_i^2}{\nu_i}\ DP$	A-3

* A_i = total molecular surface area of species i; $\gamma_{w,i}$ = surface or interfacial tension of solvent water in presence of solute S_i or adsorbent C, or S_iC; N= Avagadro's number: $W = [1 - (K^s_i/K^e_i)]$ $[(d\ell n\gamma/d\ell nT) + 2/3\ \Omega_i T]$; Ω_i = liquid thermal expansion coef of the species i; $K^{e(s)}_i$ = ratio of energy (entropy) required to form cavity of for species i with A_i in solvent to that of expanding a planar surface of solvent of same area $(A_i\gamma)_{e(s)}$; $K^e_i = 1+(K^e - 1)\ (V/V_i)^{2/3}$. K^e is K^e_i for neat solvent; V,V=molar volumes of solvent and species i; Note: K^e_i, $K^s_i \to 1$ as $d_i/d > 1$, $W \to 0$ where d,d_i = diameter of solvent, solute species. Also, when $K^e_i \sim K^s_i$, $W \to 0$ for water in particular.

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Footnotes (continued)

† $\Delta_i = 1.35\ I_i I/(I_i+I)$; I, I_i = ionization potentials for solvent, species i, D_i = Clausius-Mosotti function = $(n_i^2-1)/(n_i^2+2)$; D for solvent, n, n_i = refractive index of solvent, species i; $-f(\xi,\ell)$ $B_{ij} \approx [(0.546 \times 27)/8\pi\ (Q'+Q")]$, $Q" < 0.1Q'$, neglect Q", $Q' = \nu_i([\bar{\sigma}^6/(\bar{R}-\ell)^9]$ $[t^2/11 + t/5 + 1/9)] - [1/(\bar{R}-\bar{\ell})^3]\ [t^2/5 + t/2 + 1/3])$ where $t = \bar{\ell}/(\bar{R}-\bar{\ell})$ where Q', Q" dimensionless functions from pair potentials, $\bar{R} = 1/2\ (R_i + R)$ = mean diam, $\bar{\ell} = 1/2(\ell_i+\ell)$ = Kihara parameter, $\bar{\sigma} = 1/2$ $(\sigma_i+\sigma) \equiv$ London parameter; $R_i = 1.74\ [3v_i/4\pi^{1/3}]$; $\ell_i = R_i[(0.24 + 7\omega_i)$ $/(3.24 + 7\omega_i)]$, $\sigma_i = [R_i/1.74\ (4.64/3.24+7\omega_i)]$; ω_i = acentric factor of i.

‡ μ_i = static dipole moment of i, $\mathcal{D} = [2(\varepsilon-1)/2\varepsilon+1]$, ε = static dielectric const. of the solvent, $P = ([4\pi\varepsilon_0(1-\mathcal{D}(a_i/v_i)])^{-1}a_i$ = polararizability of i, ε_0 = permittivity constant.

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APPENDIX B

ASSUMPTIONS FOR ADAPTING THE SOLVOPHOBIC THEORY TO THE ASSOCIATED ADSORPTION REACTION

For AC adsorption, the solvent molecules (water) and their cavity surface area are usually significantly smaller than the solute molecules and their cavity surface area and the exposed nonpolar surface area of the activated carbon. Then the following assumptions appear to be reasonable [16]:

$$\mu_C = 0 \text{ (nonpolar carbon)} \tag{B-1}$$

$$\mu_{S_iC} = \mu_{S_i} \text{ (solute could be polar)} \tag{B-2}$$

$$W_{S_iC} = W_{S_i} = W_C = W_C = 0 \text{ (if } K_i^s = K_i^e \text{ or if } d_i d > 1) \tag{B-3}$$

$$\Delta G_{vdw,S_iC} = \Delta G_{vdw,C} \text{ (dilute solute concentration)} \tag{B-4}$$

To simplify the algebra, it is convenient to express the molecular volume of the carbon-solute complex S_iC as a multiple of the solute molecular volume

$$\nu_{S_iC} = \lambda \nu_{S_i} \tag{B-5}$$

where λ is the proportionality factor. For HPLC, Horvath, et al.[23] estimated λ to be about 3.7. In the equations in the text, the ratio $(\lambda-1)/2\lambda$ appears and varies in value from 0.25 to 0.5 as λ varies from 2 to infinity. Therefore, the choice of the value of λ will have a relatively insensitive effect on $\Delta G^{assoc}_{(solvent)}$ if the electrostatic term is relatively small.

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